SYNERGISTIC EFFECTS OF ADDITIVES TO BENZOTRIAZOLE SOLUTIONS APPLIED AS CORROSION INHIBITORS TO ARCHAEOLOGICAL COPPER AND COPPER ALLOY ARTEFACTS

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To my father for his faith in me and
my mother and sister for their love and
support

Synergistic effects of additives to benzotriazole solutions applied as corrosion inhibitors to archaeological copper and copper alloy artefacts

Stavroula Golfomitsou

Abstract

Benzotriazole (BTA) is a corrosion inhibitor extensively used for the stabilisation of active corrosion of archaeological copper and copper alloys. However, BTA often fails to effectively retard corrosion when applied on heavily corroded artefacts. Although there are numerous studies about its mode of action on clean copper, there is no comprehensive understanding about the way it is bonded to corroded copper. This thesis aimed to understand and compare BTA and its mode of action on clean and corroded copper by examining possible factors that could affect efficiency including concentration, solvent, period of immersion and pH. BTA efficiency could be improved by making use not only of these results but also of the synergism that is observed between BTA and other inhibitive compounds. The combination of inhibitors and the use of the synergistic effect between compounds is common in industry but has never been tested before for use in conservation. The synergistic effect could be beneficial for use on corroded copper alloys suffering with active corrosion. The six compounds selected were 5-Amino-2-Mercapto-1, 3, 4-Thiadiazole (AMT), Benzylamine (BZA), Ethanolamine (ET), 1-Phenyl-5-Mercapto-Tetrazole (PMT), Potassium Ethyl Xanthate (KEX) and Potassium Iodide (KI). These were tested on their own and in combination with BTA. Accelerated corrosion tests were carried out on artificially corroded copper coupons. Analysis using SEM-EDS, XPS, and FT-IR allowed a better understanding of the way different factors affect the formation of the copper-BTA complex formed and subsequently the BTA efficiency. The addition of other compounds into the BTA solutions significantly affected the complex formed and the film properties. Copper(I)-inhibitor complexes were proven to be more protective than copper(II) complexes. The results also showed that there is a synergistic effect between BTA and AMT which results in improved inhibitive efficiency of both inhibitors. The composition of the film formed was mainly dependent on the concentration of the solution, however, it was found to be effective in very low concentrations as well as aqueous solutions. Finally, field trials of some of the more effective solutions of compounds were performed on archaeological objects from Turkey and Greece and these results confirmed those of the laboratory experiments. All of the experiments and fields trials were designed and analysed statistically.

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CHAPTER 1

1 Introduction

Archaeological artefacts are all subject to deterioration, the type and severity of which is dependent on many interrelated factors. These include: the material composition of the object, the environment to which it has been exposed and previous interventions such as conservation or restoration treatments. Together these make up the history of the object which is key to understanding both the object and its current state of preservation. Every archaeological object should be considered uniquely valuable and its conservation should include special consideration of its preservation state, which can be equally distinctive. The objective of a conservation treatment is to reinstate the significance of the object, retard the deterioration processes, and prolong its life as long as possible (France-Lanord, 1996: 277, Wagner *et al*, 1998: 80).

The principal manner of deterioration for archaeological metal artefacts is through corrosion. Corrosion is defined as the chemical interaction of a metal with its environment. The consequences of the corrosion of metals will of course vary, however, corrosion can result in total fragmentation and "loss" of an archaeological object. Corrosion of metals can, in part, be explained in terms of their chemistry. Metals can exist in a variety of states, the stability of which differs depending on the amount of stored energy. In general, more stable states have a lower energy. The input of energy during the extraction of metals from

mineral ores reflects the fact that a metal in its elemental state is at a higher energy level, and therefore less stable than its mineral forms. Consequently, any metal object has a thermodynamic tendency to revert to more stable compounds i.e its mineral forms. These reactions represent a corresponding change in mass.

Over time a metal artefact is modified in physical and chemical characteristics, such as composition and form, alter through irreversible processes, which can result in the loss of very important archaeological information. In a burial environment, metals reach equilibrium with their surroundings and the observed rate of their corrosion can gradually slow down. Consequently, however, any alteration of the environmental conditions to which a metal is exposed disturbs this equilibrium, causing an acceleration of the corrosion rate and further changes in mass and corrosion products (Bercudou, 1996: 249).

The recognition of metal corrosion as a severe problem is by no means a modern preoccupation, and methods to reduce its progress date back to antiquity. As long as 4000 years ago, Minoans were known to treat their copper objects with oil or animal fat to restore their lustre. The use of these materials may relate to the fact that they are slightly acidic. As a result, in addition to giving a gloss finish to the object, they may also partially dissolve surface metal oxides, which dulls the appearance of the metal and seals the surface from the environment (Skoulikidis, 1991: 7). Similarly, it is evident from the construction techniques used at the temple of the Parthenon, at the Acropolis in Athens that there was a clear understanding of the performance characteristics of the materials employed. To give structural support to the marble columns, lead coated iron clamps were used. Corrosion

induced expansion of the iron would have caused the stone to rupture and this measure would have prevented the iron core from corroding.

The corrosion process can be retarded by either indirect or direct intervention. Indirect intervention (also termed preventive intervention) relies on the alteration of the environment to which an object is exposed. Direct or remedial intervention involves treatments carried out on the object itself. Preventive conservation utilises storage conditions that retard deterioration, in this case corrosion, by environmental control. For copper this is generally achieved either by the removal of oxygen, which could further oxidise copper compounds, or by reducing the water vapour content of the air, which could cause further dissolution of the metal. The removal of oxygen requires special equipment to maintain an inert atmosphere, this is not easy to achieve, especially for bigger objects. Desiccation is technically more feasible, often achieved by placing objects within inert sealed plastic boxes containing silica gel, or by the use of dehumidifiers in storage (Cronyn, 1996: 227). However the maintenance of an "inert" environment is not always possible, and is particularly problematic in the case of heavily corroded artefacts which may in fact represent the source of the problem due to chloride incorporated into the corrosion layers. Very low values of relative humidity (RH) are often required (<35%), depending on the degree of corrosion, and the composition and porosity of the corrosion products present. More importantly, post-excavation changes are not solely limited to further corrosion of the residual metal, but can also affect the existing corrosion products, the behaviour of which is also environmentally dependant. Therefore the selection and maintenance of a stable environment is difficult, and cannot always promise the long-term stability of an object.

One of the most severe types of corrosion suffered by copper and copper alloy artefacts is so-called 'bronze disease'. This is a form of localised active corrosion the mechanism of which starts when chloride-containing copper and more specifically cuprous chloride (nantokite) is exposed to moisture and air. The presence of nantokite causes the copper object to become chemically unstable, producing very characteristic corrosion products of light green, powdery spots composed principally of atacamatite and paratacamite (Scott, 1990: 193). The powdery form of the products causes loss of surface detail, which then has to be stabilised in order to prevent further disruption and disfigurement of the original artefact.

A number of methods have been used to confront this problem, the choice of which has to be based on the individual compositional characteristics of the object, as well as its condition. Certain treatments rely on the removal of original, but altered material from the object, either by stripping the entire corrosion layer; or by selectively removing corrosion agents such as chlorides.

Stripping techniques, such as electrolytic and electrochemical methods, with or without the use of chemical reagents (e.g. citric acid), have been used in order to remove the corrosion products leaving only the metal core (Rodgers, 2004: 114-115). The aim of these is to remove the 'harmful' corrosion products (e.g. nantokite). However, these methods for historical metal objects are not generally accepted for archaeological metal artefacts, since valuable information relating to history and authenticity of the object is preserved within the corrosion products. Evidence of the structure, decorative components and original use

of the object, as well as preserved organic materials (such as textiles or wood surviving in a mineralised form) could be lost forever. Importantly certain surface products which would be lost in this treatment could have been formed by ancient patination techniques (Wagner *et al*, 1998: 80). Finally, not all of the corrosion products are "harmful" for the object, but may actually protect it in part from further corrosion.

Washing techniques using distilled or de-ionised water have also been employed to remove chloride ions from the metal surface and its corrosion products. Unfortunately, cuprous chloride is not very water soluble and so the success of these treatments is limited. Moreover, washing artefacts is time consuming, requiring 2-4 years to be "effective", and importantly could cause further damage, by oxidising the residual metal (Taylor and MacLeod, 1985: 100).

To stabilise artefacts without removing corrosion products is much more difficult. One of the most well known and commonly used techniques for achieving this is by treatment with sodium sesquicarbonate. This method relies on the dissolution of nantokite underneath the corrosion crusts and is preferable for heavily corroded artefacts, where corrosion is more severe and widespread. Nantokite in contact with water reacts to give atacamite/paratacamite. In the case of sodium sesquicarbonate the presence of OH^- in the solution results in the conversion of nantokite into cuprite. During the process there is the formation of malachite precipitating on the surface. While seemingly ideal, this method faces many practical disadvantages as it is time consuming and can require years to become effective. The object is immersed into the solution for long periods. The chemical alteration

of the corrosion products is another disadvantage. Furthermore, the reactions that take place initially could cause damage to the object in the long term. Finally, a number of secondary by-products, such as chalconatronite are formed on the surface causing discoloration of malachite (Oddy and Hughes, 1970:173, Drayman-Weisser, 1987: 106, Cronyn, 1996: 229).

Another once popular method used for the stabilisation of active corrosion is silver oxide. Silver oxide was widely used in the past for the local stabilisation of bronze disease pits. The exact process has been described by Organ (1963). The corrosion pits containing atacamatite/paratacamite are excavated to expose the nantokite, to which pure silver oxide, moistened with alcohol, is applied. The object is then exposed to 78% relative humidity (RH) for about 24 hours during which time silver chloride is produced. This acts as a seal to encapsulate the nantokite. If silver chloride has been formed no new corrosion is visible after treatment. However, should this not be the case, corrosion pits will again appear, and the process has to be repeated. This method presents many drawbacks. Firstly, it stabilises only part of the surface, without intervening on the nantokite underneath. Secondly, the corrosion pits have to be excavated in depth, to allow the reagent access to the nantokite. This is not always possible, as the size of the pits depends on the stage of corrosion and the removal of powdery atacamite/paratacamite can be difficult and time consuming. Thirdly this treatment results in a visual alteration of the object, as the colour of the treated pits changes to a dark brown. Finally, one of the most important disadvantages is that future analysis of the metallic composition and original technique of the object is compromised by

the presence of modern silver (Organ, 1963: 8, Organ, 1977:126, Plenderleith and Werner, 1971: 253).

The use of chemical compounds as corrosion inhibitors in the conservation of metals dates back to the late 1960's when Madsen (1967: 163-166) first suggested the use of benzotriazole (BTA) for the stabilisation of bronze disease. As is so often the case in conservation, and particularly at that time, BTA was presented as a "wundermittel" that would solve the previously intractable problems of copper conservation. The object was immersed in an aqueous or alcoholic BTA solution, for 24 hours, with or without a vacuum. If the bronze disease was not stabilised the treatment was repeated. In comparison with the previously mentioned techniques, BTA is easy and fast to apply, and more importantly does not have the drawbacks of other methods, as it does not require removal of the corrosion products, nor does it change the metallic composition of the object (Sease, 1978: 76-85). BTA is classified as both an anodic and cathodic inhibitor.

The use of BTA was first based on a more empirical assessment of its effectiveness and the concentration and time of immersion varied depending on a number of variables. For example, a collection of bronzes in Thailand were treated with 1-3% BTA in alcohol and 1-2 % in water during a large project carried out during the 1960s. Objects were immersed into the solution for a few days or at least overnight (Bacon and Janposri, 1977: 37). This latter practice does not differ from current museum applications.

The reaction of BTA with copper corrosion products, especially with nantokite has always been of great interest in conservation. Tennent and Antonio (1981) found that the complex formed between BTA and cuprous chloride was not stable and after seventy two hours it was converted to BTA-atacamite complex suggesting it is a subject for further investigation.

The importance of corrosion inhibitors in conservation was also highlighted in a conference held in 1984 by the British Museum and Museum of London and published in 1985. In that publication issues regarding corrosion inhibition theory as well as inhibitors used for copper and iron were discussed (UKIC Occasional Papers, 1985, Number 4).

More systematic research into benzotriazole and its function on archaeological copper has been undertaken recently (Brostoff, 1997, Faltermeier, 1995, Mohamed *et al*, 2004, Golfomitsou and Merkel, 2004) with particular emphasis on its action when used on corroded surfaces. For example, Brostoff (1997) examined the Cu-BTA complex formed on different corrosion products.

The effect of BTA on other metals has also been of concern. Sharma et al (2003: 203-309) examined the effect of BTA on leaded bronzes suffering pitting corrosion of lead rather than copper. Of particular interest is the effect of the pH on the process. It was found that at neutral pH BTA forms a protective complex with lead, therefore, BTA was neutralised to pH 7 using calcium carbonate. The BTA concentrations used were 0.5% applied by immersion for two days, or by brushing four coats of 1%. The film formed was found to be

a stable Pb-BTA polymer in a stoichiometric ratio 1:2 and appeared to provide protection against organic acid fumes.

Still the exact mechanisms of BTA on corroded copper are not known and it is one of the key questions of this thesis. Benzotriazole is not fully effective in the treatment of heavily corroded artefacts. However, it is worth mentioning that BTA is used in many different ways. The reasons of its partial failure could simply be related to inappropriate application methods. For example, it has been reported that because BTA works better at near neutral pH values failing to stabilise corrosion at very acidic values ($pH \leq 2$), as is the case in the active corrosion pits, copper objects should not stay immersed in the BTA solution for long periods as this could result in pH drop with detrimental consequences. However, there has never been much study regarding the pH drop and/or the efficiency of the treatment to provide further information that could be translated into practical application methods especially for conservation of archaeological copper and copper alloys. Therefore, reports on BTA inefficiency can be related to a number of undefined reasons. This particular issue of the BTA "failure", the pH of the solution the time of immersion, and their effect on the film formed were issues that required further investigation which this research will address.

Research on corrosion inhibitors has been predominantly undertaken for industrial applications. These involve the treatment of corrosion-free copper surfaces, and consequently the majority of corrosion inhibitors tested to date have been designed for non-corroded metal surfaces. While there is an extensive literature on corrosion inhibitors, very little of this bears any relevance to the use of these materials on archaeological artefacts.

The fact that conservation requirements are very different to engineering requirements is reflected in the fundamental disparity of approach taken by conservation and industry towards the protection of metals. Nevertheless, in the last decade there has been an increased interest in the use of BTA and the manner of its function on different corrosion products for conservation purposes.

The aim of this research was to investigate further the function of selected industrial corrosion inhibitors on corroded copper artefacts. Corrosion inhibitors act by forming a complex with copper and/or chloride ions to form a surface polymeric film that could protect the object from its corrosive environment. The use of selected combinations of corrosion inhibitors rather than just using one inhibitor at a time is one of the most promising techniques available for the stabilisation of active corrosion. Importantly for historic artefacts, the organic corrosion inhibitors upon which this research is focused do not affect on the composition of the metal alloy.

As a first step, the stabilisation of artificially corroded copper coupons with benzotriazole and other inhibitive compounds were examined in order to gain a better understanding of the mechanism of their action on heavily corroded surfaces. Following this, methods to improve the beneficial effect of benzotriazole on copper were investigated. This focussed on the development of improved application methodologies, and also the alteration of the reagent solution through the use of additives. The theory and experimental data that have been published to date refers to clean metal surfaces, and the experimental procedures by which these materials have been tested cannot be applied for testing inhibitors for

archaeological copper and copper alloy objects. One particular issue for investigation was the synergism that some inhibitors exhibit when used in conjunction with each other. In certain situations the inhibitive efficiency of inhibitor mixture may be greater than the sum of each one of the additives. Consequently, it is common practice in industry to use more than one corrosion inhibitor for the protection of metals. On the basis of an extensive literature review six inhibitors were selected to examine in combination with BTA for potential application on archaeological copper and copper alloy artefacts. This positive synergism between different inhibitors relies on the utilisation of specific characteristics of the different inhibitor compounds that complement the mode of action of the other agents present. For example, as has already been mentioned, BTA is not effective at acidic pH values, which are typically encountered on archaeological metal surfaces. The addition of amines to the BTA solutions results in neutral or slightly alkaline pH values, thus theoretically improving the inhibition function of the BTA.

Of great importance is the manner in which these inhibitors chemically and physically interact with corroded copper surfaces. Therefore accelerated corrosion tests were carried out in order to test the performance of these new compounds under extreme relative humidity conditions (95±5 %). However, methods of analysis, such as electrochemical techniques, that are typically used to measure the corrosion rate of inhibited and uninhibited copper are not readily applicable to corroded surfaces. Consequently, the behaviour of inhibitors on complex corroded surfaces is difficult to assess. An objective of this research was to investigate the way in which inhibitors are bonded to the metal surface. SEM-EDX analysis, Infrared Spectroscopy (FTIR) and XPS were employed to examine the thickness

and physical characteristics of the film that is formed and its polymerisation with copper ions, factors of great significance for the effectiveness of inhibitors. Through a better understanding of the inhibitive mechanisms, as well as of the physical attributes of films in corrosion layers, it is possible to adopt a more informed approach to the selection of treatment agents. Importantly, the effectiveness of the compounds used can be optimised by the development of suitable application methodologies. Therefore the behaviour of these compounds on two different substrates, using different media and application methods (e.g. time of immersion) was investigated.

Initial bench tests were carried out with several inhibitive compounds that could possibly work on corroded archaeological copper. Not all of the compounds involved in these tests were included in the main experiments. One of these compounds was 4-methyl-imidazole which is considered an "eco-friendly" compound. Imidazoles include a great variety of compounds acting as corrosion inhibitors for copper. However, the preliminary tests with 4-methyl-imidazole showed that the compound caused major colour alterations (the cuprite surface turned bright green), also the film was not adherent on the copper substrate, showing there was not sufficient bonding with copper and finally, after twenty-four hour exposure to 95±5%RH the film flaked off completely. Weight change measurements showed acceleration of corrosion.

With regards to the analytical section of the work, it is worth mentioning that several tests were carried out with a variety of techniques, including Raman Spectroscopy, Static SIMS, Cyclic Voltametry and Potentiometry. Some of the techniques gave satisfactory results (e.g.

Cyclic Voltametry, potentiometry) whilst other were not considered suitable for the specific analysis and are not reported in this thesis.

One of the most important issues in this research was to follow a systematic approach in the testing and analysis of new compounds that could be used for conservation purposes. The investigation of new methods or compounds for the conservation of metals requires a good understanding of a variety of topics, such as corrosion of metals and physicochemical properties of the corrosion products, chemistry of the materials used and their possible interaction with a metal surface and finally comprehension of the conservation aims in terms of treatment requirements, aesthetic and ethical considerations. Often different researchers focus on different aspects of the field, the merging of which is a major challenge faced in this study.

The designing of treatments anew is not a straightforward task because of the plethora of compounds already existing. Understanding the function of certain inhibitors on a variety of corroded surfaces might help in the further investigation of more effective, eco-friendly compounds. It is essential to assess the synergistic effect between the selected compounds as well as their reactions with copper. It is not always possible to comprehend in full all of the reactions leading to a metal-inhibitor film formation. However it is vital to examine how the film is formed, its chemical composition and subsequently its properties. These can then be related to the efficiency of the treatment in order to advance further in this research.

Corrosion inhibition is directly related to corrosion and its principles. Therefore, the second chapter discusses basic thermodynamic and kinetic principles of copper corrosion processes. Following this, fundamental aspects of corrosion inhibition principles, factors affecting the inhibitive mode of action are discussed. The synergistic effect observed between different inhibitors and has been used for this research is also discussed in chapter 3. In the same chapter, corrosion inhibitors used in conservation, including benzotriazole are discussed and the chapter concludes with the new compounds used for this study.

Chapter 4 discusses the methodology followed. The experimental designs, the accelerated corrosion testing and coupon preparation as well as the archaeological field testing methods are discussed in full. The results of the laboratory experiments are divided into two chapters. Chapter 5 investigated how the efficiency of BTA is affected by selected variables. Analysis of the copper-BTA film formed on the surface furthered the understanding of its function on clean and corroded copper. Chapter 6 examined six new compounds that have been reported to exhibit a synergistic effect with BTA. A series of different experiments and further instrumental analysis were employed to get an insight into the way they interact and work together. Chapter 7 discusses the testing of selected inhibitor solutions carried out on real archaeological objects. In chapter 8, the results of the laboratory and field tests are examined. Finally, the conclusions of this research are listed along with suggestions for further research in the field of corrosion inhibitors and the use of synergistic effect in conservation.

CHAPTER 2

2 Corrosion of Copper and Copper Alloys

2.1 Introduction

Corrosion inhibition is a method used to retard the corrosion process of a metal or alloy by adding chemical compounds to a metal or its environment. Corrosion inhibitors have had long-standing application in industry, commencing in the 19th century with the use of plant extracts (Sastri, 1998:26). In the conservation of metal antiquities inhibitors are currently extensively used, in particular for the stabilisation of copper and copper alloy artefacts.

Chemical compounds that could potentially function as inhibitors for copper are numerous. For example, theoretically even agents that normally promote corrosion (such as chloride anions, etc) could actually prevent this process if present in specific concentrations (Fontana, 1986: 198).

Corrosion is related to the interaction of a metal with its environment, therefore, the major issues to be considered when discussing corrosion are the metal (composition, structure, properties), the environment (chemical composition and nature) and their interaction (Shreir *et al*, 1994). The majority of metal corrosion reactions take place through electrochemical processes. Corrosion inhibition should not be studied independently but in relation to actual corrosion mechanisms. A definition of the electrochemical aspects of corrosion can help in a better understanding of the complex mechanisms of corrosion

inhibition. Therefore, some fundamental issues and the electrochemical principles of corrosion will be discussed first. In the following chapter the way that corrosion inhibitors work will be discussed. Next a review of the theories on corrosion inhibitor action will be presented. The classification of the inhibitors, according to the way they act, or their chemical composition, is considered of great importance as it groups the effects that inhibitors have on metals corrosion. Finally, the inhibitors that have been used or tested for use in the conservation of archaeological copper and copper alloy artefacts will be examined.

2.2 Corrosion Fundamentals

Corrosion develops through a series of electrochemical reactions which take place between a metal and its environment. During this process electrons are transferred, through either an aqueous or a solid electrolyte, causing corrosion of the metal. While the tendency of a particular metal to corrode can be determined thermodynamically, the rate at which this will take place is dependent on the kinetics of the various reactions involved.

2.2.1 Thermodynamics of Corrosion

The deterioration of metals, such as archaeological copper artefacts, is essentially the result of the transfer of electrons from the metal to the oxidising agent, during which the metal becomes oxidised.

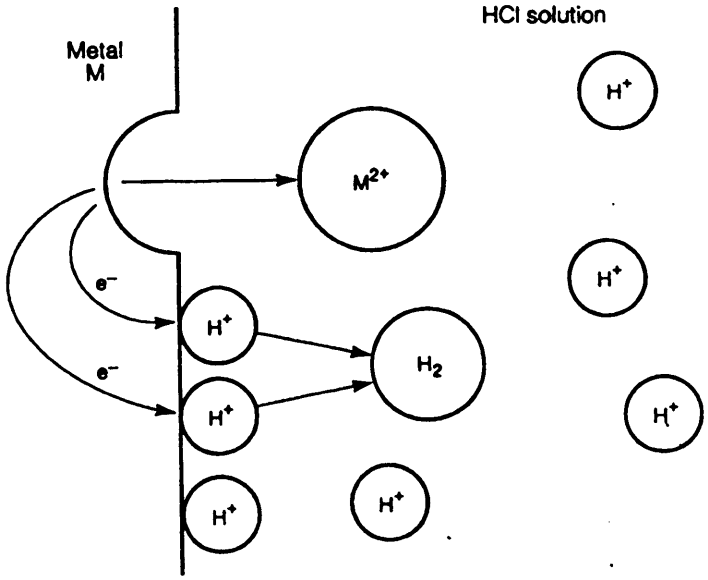


Figure 2.1. Metal dissolution in HCl solution (after Jones, 1996: 6).

This process can be considered in terms of two half reactions, one anodic and the other cathodic, in electrical contact with an electrolyte. The anodic reaction is the oxidation of the metal (resulting in an increase of valence) while the cathodic is the reduction of the oxidising agent (which experiences a decrease in valence). In neutral solutions the oxidising agent is predominantly oxygen. Thus it can be seen that corrosion is the result of electron transfer. The anodic reaction (1) liberates electrons which are then consumed by the cathodic reactions (2, 3). Consequently the rates of the anodic and cathodic reactions are the same (Fontana, 1986: 15).

$$M \rightarrow M^{n+} + ne^- \text{ (anode)} \quad (1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (cathode in neutral solutions)} \quad (2)$$

In acidic conditions (pH< 7) the cathodic reaction results in the evolution of hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (cathode in acidic solutions)} \quad (3)$$

Owing to its variable oxidation state, the oxidation of copper takes two steps: (Fiaud, 1995:930-931)

$$Cu \rightarrow Cu^{+} + e^{-} \quad (4)$$

$$Cu^{+} \rightarrow Cu^{2+} + e^{-} \quad (5)$$

Consequently, there are also several different anodic reactions. In addition to promoting an initial oxidation of copper metal, dissolved oxygen will further oxidise Cu^{+} to Cu^{2+} according to the reaction:

$$2Cu^{+} + 1/2O_2 + H_2O \rightarrow 2Cu^{2+} + 2OH^{-} \quad (6)$$

Similarly, in the presence of ions such as Cl^{-}, the anodic reactions are:

$$Cu + Cl^{-} \rightarrow CuCl + e^{-} \quad (7)$$

$$CuCl + Cl^{-} \rightarrow CuCl_2^{-} \quad (8)$$

The tendency of metals to corrode is given by the Electromotive Force Potential Series (EMF). This series represents the reduction reaction of a metal, relative to hydrogen reduction, in what is called standard hydrogen electrode (SHE). The hydrogen electrode potential is arbitrarily defined as zero. Metals that are oxidised more easily than hydrogen have negative values, those that do not have positive values. In general, the more negative the potential value is, the more reactive the metal (active metals), and the more positive the value, the less likely it is to corrode (noble metals). These reactions are measured in volts, and the values represent the equilibrium potential of a metal with its ions, at a 1 M ionic concentration, at 25 °C, and 1 atm pressure. When two metals are in contact, the metal with the lower potential in the electrochemical series acts as the anode while the more positive is the cathode. This is covered in textbooks on corrosion, such a Craig (1991), Jones, (1996), Uhlig and Revie, (1985), and Evans (1981).

Table 2.1. Electromotive Force Potential Series (EMF) (after Craig, 1991: 6).

	Reaction	**Standard Potential**, in 25° C, (Volts)
	$Au^{2+} + 2e^- = Au$	1.70
Noble		
	$Au^{3+} + 3e^- = Au$	1.50
	$Pt^{2+} + 2e^- = Pt$	1.2
	$Pd^{2+} + 2e^- = Pd$	0.987
	$Hg^{2+} + 2e^- = Hg$	0.854
	$Ag^+ + e^- = Ag$	0.800
	$Cu^+ + e^- = Cu$	0.521
	$Cu^{2+} + 2e^- = Cu$	0.337
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	-0.126
	$Sn^{2+} + 2e^- = Sn$	-0.136
	$Ni^{2+} + 2e^- = Ni$	-0.250
	$Co^{2+} + 2e^- = Co$	-0.277
	$Ti^+ + e^- = Ti$	-0.336
	$Cd^{2+} + 2e^- = Cd$	-0.403
	$Fe^{2+} + 2e^- = Fe$	-0.440
	$Cr^{3+} + 2e^- = Cr$	-0.744
	$Zn^{2+} + 2e^- = Zn$	-0.763
	$Cr^{2+} + 2e^- = Cr$	-0.91
	$Mn^{2+} + 2e^- = Mn$	-1.18
	$Zr^{4+} + 4e^- = Zr$	-1.53
	$Ti^{2+} + 2e^- = Ti$	-1.63
	$Al^{3+} + 3e^- = Al$	-1.66
	$Mg^{2+} + 2e^- = Mg$	-2.37
	$Na^+ + e^- = Na$	-2.71
	$K^+ + e^- = K$	-2.93
	$Li^+ + e^- = Li$	-3.05
Active		

While the EMF potential represents the tendency of a metal to corrode, this does not necessarily reflect the rate at which this could happen. All metals, under certain conditions, will corrode. When metals are oxidised their potential becomes more positive, conversely

when a metal undergoes cathodic dissolution, its potential becomes more negative. This is referred to as anodic and cathodic polarisation (Evans, 1960:287).

Table 2.2. Galvanic Series in Seawater (after Jones, 1996: 14).

Cathodic(noble)
↑
Platinum
Gold
Graphite
Titanium
Silver
Zirconium
AISI Type 316, 317 stainless steels
AISI Type 304 stainless steels
AISI Type 430 stainless steels
Nickel
Copper-Nickel (70-30)
Bronzes
Copper
Brasses
Nickel
Naval Brass
Tin
AISI Type 316, 317 stainless steels
AISI Type 304 stainless steels
Cast iron
Steel or Iron
Aluminium
Cadmium
Zinc
Magnesium and Magnesium Alloys
↑
Anodic

In addition to the SHE, there are many other reference electrodes that can be used to measure the tendency of metals to corrode, these include the calomel electrode and the silver/silver chloride electrode.

One drawback to the EMF is that is refers only to pure metals. As mentioned above, different metals have different corrosion potentials. If two metals are in contact, or within

the same alloy, then the metal with the more negative corrosion potential will undergo preferential corrosion. This behaviour is reflected by the galvanic series, which represents the reactivity of an alloy in a given environment. Table 2.2 gives the galvanic series for alloys in seawater. However, the order of reactivity of these alloys in different natural environments does not present any major deviations (Jones, 1996: 12).

A second problem with the EMF is that it does not follow alterations of the metal to intermediate states. In such situations the potential of the reduction reaction is no longer the same as the equilibrium potential referred to in the electromotive force series.

2.2.2 Nernst Equation

The corrosion conditions differ from those used to describe half reactions in EMF series. These deviations from the standard conditions can be calculated by the Nernst equation, which links the standard electrode potential E to Gibb's free energy. For the equation:

$aA + mH^+ + ne^- \rightarrow bB + dH_2O$, the potential can be calculated according to the equation:

$$E = E^\circ\ RT/nF.\ln(B)^b(H_2O)^d/(A)^a(H+)^m \quad (9)$$

It can also be expressed as:

$$E = E^\circ + 2.3RT/nF.\ \mathrm{Log}\ (A)^a(H+)^m/(B)^b(H_2O)^d \quad (10)$$

Where R is the gas constant, T is temperature, n is the number of electrons and F is Faraday's constant. The second expression of Nernst equation shows that the potential becomes more positive (noble) when the oxidation increases (Jones, 1996).

2.2.3 Corrosion potential

The potential changes of a metal can be measured in a simple cell using a voltameter with respect to a reference electrode. The measured potential is called corrosion potential and it refers to the combination of half reactions occurring. The corrosion potential depends on the kinetics of these reactions. It is used in combination with Pourbaix diagrams as an indication of the activity of a metal. Corrosion potential alone cannot provide information about the corrosion rate (Jones 1996).

Corrosion potential measurements are easy to perform and are used in the conservation of metals to monitor conservation treatments such as stabilisation of marine metal artefacts (Degrigny and Spiteri, 2004).

2.2.4 Potential-pH

Another method for measuring the thermodynamic tendency of a metal to corrosion is the use of potential-pH diagrams. These are charts plotting the equilibrium potential against pH of a solution. Potential-pH diagrams can be used to predict whether or not corrosion, *passivation* or *immunity* of a metal in an aqueous environment is thermodynamically possible. Immunity refers to the state of the metal where corrosion is energetically impossible to occur in a given environment. If the metal is in a passive state corrosion is not impossible, however its surface is covered by a film of oxides or hydroxides. The degree of corrosion which is possible is dependent on the nature of the corrosion products already formed and the porosity of the film. Pourbaix (1966: 16) studied the reactions and the corrosion products of a metal in equilibrium with its ions in aqueous solutions, taking into account its potential and the pH of the solution. The potential-pH diagrams are often

referred to as *Pourbaix diagrams* and are used in textbooks of corrosion as fundamental diagrams to compare reactions to these two variables (Evans, 1960: 247).

These diagrams provide a useful tool for studying the behaviour of a metal in a corrosive system, as they give an indication of the electrochemical reactions that could take place and the corrosion products that are formed. Importantly, these diagrams illustrate the passive or immune areas in a given system, so that the potential of a metal or the pH of the solution can be adjusted in order to prevent corrosion (Jones, 1996: 80).

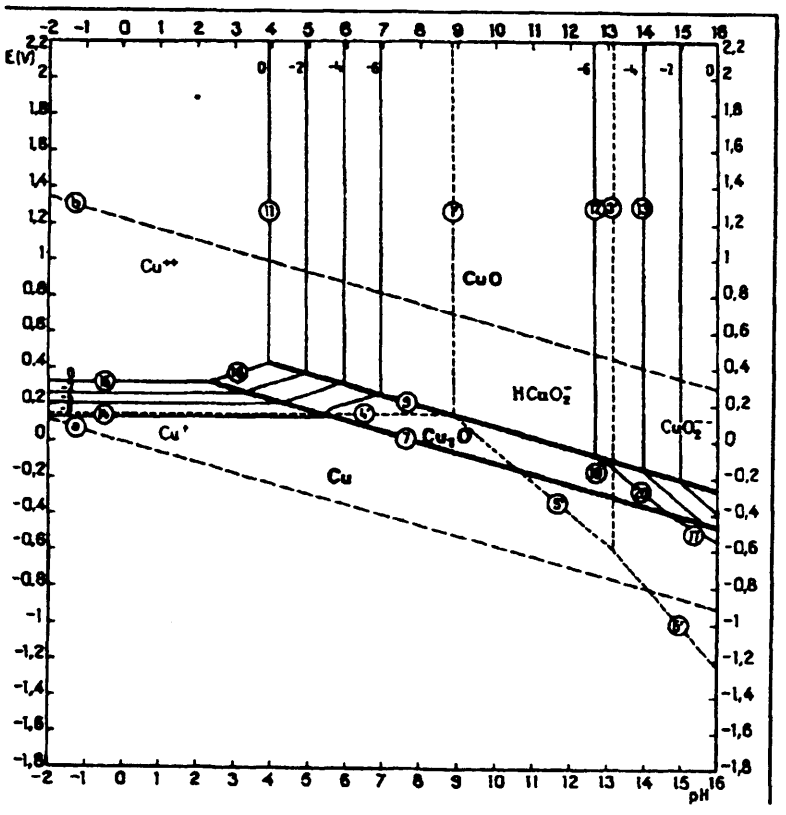


Figure 2.2 Potential-pH diagram for copper ***(after Pourbaix, 1966: 387)***

Copper is often considered as noble because its oxidation reactions take place above the line of hydrogen reduction. Because of this, copper is thermodynamically corrosion resistant and cannot be oxidised by hydrogen or water (Jones, 1996). Figure 2.2 illustrates

the potential-pH diagram for copper, of which a simplified version is given in Figure 2.3. The CuO and Cu_2O represent the passive state, Cu is the immune state whilst Cu^{2+} and CuO_2^{2-} are in areas where corrosion is thermodynamically possible.

Although these diagrams are useful for the prevention of metals corrosion they have many limitations. Like the EMF they refer only to pure metals and thus cannot predict the behaviour of complex metal alloys or impurities. For example, the behaviour of bronze differs from brass, depending on the different composition of these two alloys. Another limitation for their use is that they are applied to metals in equilibrium with their ions, which is rarely the case in reality.

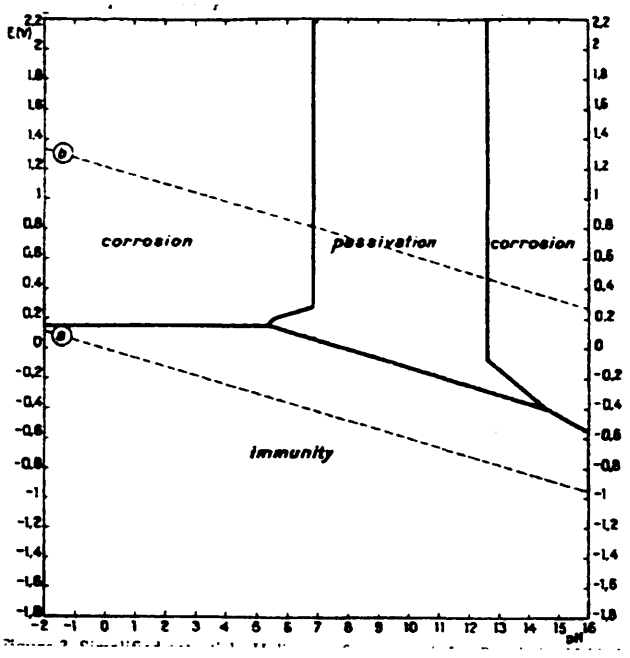


Figure 2.3 Simplified potential-pH diagram for copper ***(after Pourbaix, 1966: 389).***

Moreover, even if they give an indication of the possible reactions, they do not give information about the kinetics of these reactions, which depend on other factors. In particular, corrosion accelerators such as chloride ions are not considered. In conclusion,

the study of corrosion with the potential-pH diagrams would be complete only if the kinetics of corrosion and structural studies of the metals were also taken into account (Pourbaix, 1966: 14, 15 and Skerry, 1985: 6).

2.2.5 Electric Double layer

Metal surfaces are electrically charged. When a metal is in contact with a solution, positive metal ions migrate from the metal bulk to the surface, while negative ions from the solution are attached on the interface (Figure 2.4).

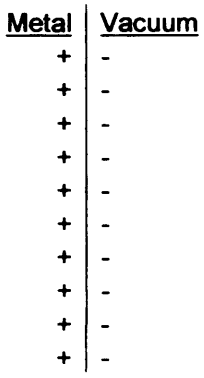


Figure 2.4 Schematic charged interface, *(after Craig, 1991: 2).*

Consequently a negatively charged surface layer covers the metal surface. In an aqueous solution, this negatively charged surface attracts water molecules, which are oriented so that the positive end points towards the metal surface and the negative end towards the solution. Other positive ions from the solution are then attracted and become attached to the negative end of the water dipoles. Thus the metal surface is covered by a monolayer of water dipoles called *inner Helmholtz plane*, whilst the positive ions from the solution, attached on the water molecules are referred to as the *outer Helmholtz plane* (Figure 2.5).

These two layers form an *electric double layer* (Craig, 1991: 2-5). If there is no excess of electrons in the double layer, then the metal has zero charge potential.

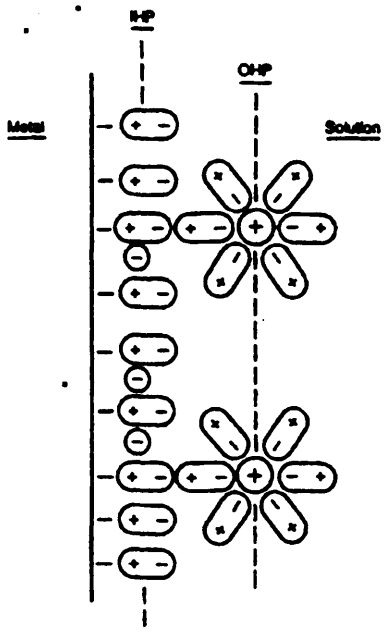


Figure 2.5 Electric double layer ***(after Craig, 1991: 4).***

The double layer is of great importance for the study of metals corrosion, as well as corrosion control. Corrosion depends on the structure and electric charge of the double layer. The formation of corrosion products is related to the adsorption of ions from the environment to the metal surface.

Ions such as chlorides are capable of displacing water dipoles from the double layer and then are easily adsorbed on the metal surface, accelerating corrosion (Shreir *et al*, 1994: 20:21). Similarly, the adsorption of corrosion inhibitors is also dependent on the double layer and the zero charge potential, and as a result this determines their subsequent film formation. The measurement of inhibitor adsorption is also studied through this layer (Rozenfeld, 1981: 120).

Since metals in reality are not in equilibrium with their environment (electrolyte) this negates the direct application of thermodynamic considerations.

2.3 Kinetics of Corrosion

The study of kinetics is of great importance because it represents the rate of the corrosion process. Conservation is primarily concerned with the deterioration of artefacts over time. Whilst the initial corrosion rate for archaeological metals can be great, over time the rate often decreases due to the development of protective corrosion products. Therefore kinetics are of paramount importance. It is of great importance to know not only if something can occur, but also how fast this will occur, and the effect that components of the metal's environment will have on the corrosion process. Corrosion is the net result of two half reactions. It therefore follows that the rate at which these reactions proceed determine the overall process. Since the anodic and cathodic reactions are mutually dependent if the rate of one increases then the rate of the other will also increase (Craig, 1991: 27).

When a metal is in contact with an electrolyte an *electrolytic cell* is formed, and electrons flow from the anode (metal) to the cathode (e.g. solution). The rate of a reaction is measured in terms of the *current* (*i*) produced by the electron flow to or from a surface. The number of the electrons transferred per unit surface area is called the *current density*, which is affected by the nature and structural properties of the metal (Jones, 1996: 76). The *corrosion rate* (*r*) is proportional to the *exchange current density* (*i*), and the Faraday's Law expresses this:

$$r_{oxid}=r_{red}= i_o/nF \quad (11)$$

where:

r_{oxid} :the equilibrium oxidation rate

r_{red} : the equilibrium reduction rate

i_o :exchange current density

n : the number of equivalents exchanged, and

F : Faraday's constant (that equals with 96.500 coulombs/equivalent)

In equilibrium, the current flow from the anode to the cathode (i_a) is equal to that which flows from the cathode to the anode (i_c):

$$i_o = i_a= i_c \quad (12)$$

The rate of the oxidation and reduction reactions when the system is in equilibrium is given by i_o which is the exchange current density (Fontana, 1986: 455).

When a metal is in equilibrium its equilibrium potential is estimated as zero. With the onset of corrosion, the potential of the metal changes to *corrosion potential* (E_{corr}). This deviation from the equilibrium potential is called polarisation, and is measured by the *overvoltage* (η), which equals the difference between the corrosion potential and the *equilibrium zero potential* ($E_{q=0}$) (Fontana, 1986: 455).

$$\eta = E_{corr} - E_{q=0} \quad (13)$$

At equilibrium the anodic and the cathodic currents are equal (Skerry, 1985: 7). When corrosion begins, the potential is shifted and the metal undergoes anodic or cathodic polarisation. The transfer of ions from the electrolyte on the metal's double layer shifts the potential chemically or electrically (Craig, 1991: 29).

The changes in polarisation (that occur during corrosion) can be studied with the aid of *polarisation diagrams*. These diagrams are based on the *Tafel equation* and are extensively used for corrosion and corrosion inhibition studies:

$$\eta = \beta \log i/i_{corr} = \beta (\log i - \log i_{corr}) \qquad (14)$$

where:

η : overvoltage

i : the current at overvoltage η

i_{corr} : the corrosion current, and

β : Tafel constant of "β slope".

The Tafel constant β is calculated separately for the anodic and cathodic reactions (β_a and β_c). The β_a and β_c Tafel constants are determined at the same time (Sastri, 1998: 78). [1] Tafel's equation shows a linear relationship between the overvoltage and the current's logarithm.

The corrosion process is described using the *mixed potential theory*, by which any electrochemical reaction can be divided into two of more half reactions. According to the mixed potential theory, corrosion can be considered in terms of two or more half reactions, which obey the *conservation of charge law* and do not result in a net accumulation of electric charge. Consequently, the total oxidation rate is equal to the total reduction rate

[1] $\beta_a = 2.3RT/anF$ and $\beta_c = -2.3RT/anF$, where

R: gas constant

T: absolute Temperature

a : symmetry coefficient

n : the number of electrons transferred

F : Faraday's constant

(Fontana, 1986: 463). This theory finds application in the construction of potential current diagrams for the study of corrosion and corrosion inhibition, first used by Evans (1960). According to this, each of the anodic and cathodic reactions has its own potential and exchange current density value.

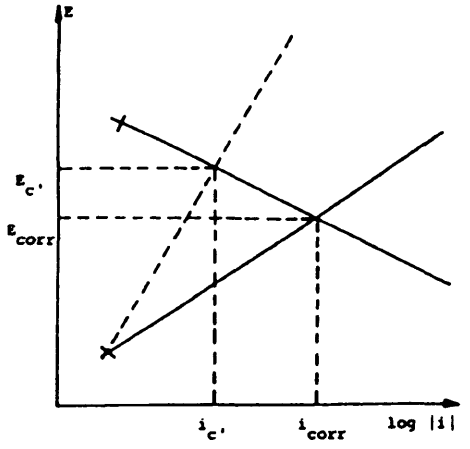


Figure 2.6. Potential current diagram of anodic polarisation *(after Skerry, 1985: 9).*

Figure 2.6 illustrates a potential-current diagram with anodic and cathodic reactions. E_{corr} is the mixed corrosion potential where the oxidation rate is equal to the reduction rate.

The potentials change according to the aforementioned Tafel equation (12). The rate of corrosion i_{corr} equals with the rate of the anodic dissolution, which is the oxidation of metal (Jones, 1996: 87).

The potential/current or *Evans' diagrams* are used for corrosion and corrosion inhibition studies. These diagrams, although experimental, can give an indication of the rate of corrosion of a metal and how other chemical compounds might affect this. Moreover, in terms of corrosion protection, these diagrams can show the mode of action of corrosion inhibitors (e.g. by retarding the anodic, cathodic, or both electrochemical reactions).

Unfortunately, these diagrams have drawbacks and limitations for inhibition mechanism studies. Theoretically all of the anions could suppress corrosion if present in specific concentrations. In practice this is not always the case. The diagrams do not give evidence for the existence of oxidising[2] inhibitors in the passive state of a metal, which in reality is not an impossibility. For non-oxidising inhibitors[3] added to a metal/electrolyte system, the current-potential diagrams present the passive state and do not give evidence for the need of the anions, as the presence of oxygen results in the formation of a passive film. The diagrams refer to each inhibitor individually, therefore they cannot be used when more than one inhibitor is added to the metal and act synergistically, as they do not take into consideration the interactions between the compounds. Finally, inhibitors could function on the interface of the metal, and interactions like these are not taken into consideration from this model. The knowledge of their limitations could result in their proper use for specific inhibitors (Skerry, 1985: 7).

Consequently, in order to gain an insight into the inhibition mechanism, it is essential to have information on the copper corrosion mechanisms, as well as the nature and physical and chemical properties of the corrosion products formed.

---

2 Oxidising are called the anodic inhibitors that can retard the anodic reaction, even in the absence of oxygen.

3 Non-oxidising inhibitors are the anodic inhibitors that retard the anodic reaction only in the presence of oxygen

2.3.1 Corrosion in different environments

As has already been mentioned, corrosion is the result of the interaction of a metal with the environment. Corrosion of copper in soil depends on a number of factors including the chemical composition of the soil, the water content, the Redox potential (which is determined by the oxygen and moisture content), the oxygen content, the pH, the amount and type of salts present and the soil resistivity. The composition of the soil alone cannot determine the corrosivity of soil. Soil corrosivity is a function of the soil resistivity and the pH used to predict the corrosion rate of a metal buried in soil. In general high moisture content in combination with a high concentration of dissolved salts and low pH results in more corrosion conditions, therefore increased corrosion. The length of time water or moisture remains resident on a metal surface affects greatly the corrosion rate of copper in the soil (Jones, 1996: 384).

Corrosion in the atmosphere is determined by factors such as the humidity, temperature and pollutants. Humidity is prerequisite for corrosion as it acts as the electrolyte in the electrochemical process. Pollutants have a great effect on the corrosion rate as they enhance the electrolytic properties of the water film formed on the metal surface. The types of pollutants vary in urban, industrial or rural environments. Typical pollutants include SO_2, NO_x, O_3 and Cl^-. Finally, the effect of temperature can vary. Low temperatures decrease the corrosion rate whilst high temperatures increase it. This can also be reversed though as high temperatures could effectively dry a metal surface, subsequently slowing down corrosion.

The combination of high humidity, high pollutants and elevated temperature can be detrimental for the corrosion of a metal (Jones, 1996: 400-402).

Corrosion in water is largely dependent on the pH of the aqueous solution. Although the anodic reaction (oxidation of metal) remains the same at all pH values, the cathodic reactions change with pH affecting the corrosion rate. The amount of dissolved oxygen in the solution also controls the corrosion rate (Jones, 1996: 357). Seawater is a more complex system, the corrosion rate depends on the salinity, the concentration and access of dissolved water to the metal, the concentration of pollutants and minor ions and biological factors. All these factors are reliant on the temperature of water, the depth at which the object is found and the current. The corrosion products and forms of corrosion vary depending on all these factors (Jones, 1996: 357, Scott, 2002: 67).

2.3.2 Corrosion forms

The corrosion rate is affected by the corrosion forms developed on the objects. Corrosion forms are related to the composition and metallurgical structure of a metal/metal alloy as well its environment. Corrosion forms are usually described based on their visual appearance following corrosion. Uniform corrosion is the corrosion where a homogeneous corrosion layer (usually cuprous oxide) is formed on the surface. Localised corrosion is corrosion developed to a restricted area and can be further divided into subforms including pitting, filiform and crevice corrosion.

Pitting corrosion is one of the most severe forms of corrosion. Pitting corrosion is an autocatalytic corrosion process. There are three main steps in pitting corrosion: the pit initiation, the early stage of pit growth and the late stage which could lead to repassivation or to uninterrupted pit development (Fischer *et al,* 1997: 90). The metal inside the pit is dissolved, producing an excess of positive copper ions. Chlorides migrate from the environment or the metal bulk inside the pit to maintain electroneutrality and nantokite is formed. Inside the pit the metal is hydrolysed resulting in low pH inside the pit. The low pH and the high concentration of chlorides have as a consequence the acceleration of corrosion (Sastri, 1998: 14-15). This corrosion mechanism, also known as "bronze disease", starts when chloride-containing copper and more specifically cuprous chloride (nantokite) is exposed to moisture and air. The presence of cuprous chloride causes the copper object to become chemically unstable.

Other forms of corrosion include selective corrosion when there is selective dissolution of a metal in an alloy. A characteristic example of selective corrosion is dezincification of copper.

2.3.3 Corrosion Products of Copper

In archaeological conservation there is a distinction between 'patina' and corrosion 'crust'. Patina is generally defined as a uniform corrosion layer that is formed slowly, which represents the original shape of the object and acts protectively towards the object. Crust is mainly referred to as any other corrosion product, which could cause instability in the condition of the object (Organ, 1992: 424, Cronyn, 1996: 216). Copper corrosion product

formation depends on many interrelated factors including the composition of the metal or alloy and the environment the object is exposed to. Metal objects of the same composition exposed to different environmental conditions will present different forms of corrosion and corrosion products, representative of their relative corrosive environment. The corrosion rate depends on all these factors. It is generally accepted that copper I oxide or cuprite is the first corrosion product formed in most environments. The properties of cuprite and colour vary dependent on impurities present, nonstoichiometry and the size of the particles. Copper II oxide or tenorite is generally less common amongst copper corrosion products (Scott, 2002: 82).

Table 2.3. Selected copper corrosion products (Scott, 2002: 418-421).

Name	Chemical Composition	Colour
Cuprite (copper I oxide)	Cu_2O	Red
Tenorite (copper II oxide)	CuO	black
Spertiniite (copper hydroxide)	$Cu(OH)_2$	Blue green
Malachite (Basic copper (II) carbonate)	$CuCO_3Cu(OH)_2$	Green
Azurite (Basic copper (II) carbonate)	$2CuCO_3Cu(OH)_2$	Blue
Chalconatronite (Sodium copper carbonate hydrate)	$Na_2Cu(CO_3)_2.3H_2O$	Greenish blue
Brochantite (Basic copper (II) sulphate)	$CuSO_43Cu(OH)_2$	Vitreous green
Antlerite (Hydroxyl copper sulphate)	$Cu_3(SO_4)(OH)_4$	Vitreous green
Nantokite (copper I chloride)	$CuCl$	Grey green(waxy)
Atacamite (Basic copper (II) chloride)	$Cu_2(OH)_3Cl$	Vitreous green
Paratacamite (γ-Basic copper (II) chloride)	$Cu_2(OH)_3Cl$	Light green
Botallackite (Basic copper (II) chloride)	$Cu2(OH)3Cl$	Light bluish green
Clinoatacamite	$Cu_2(OH)3Cl$	Pale green
Anilite	Cu_7S_4	Metallic bluish green
Chalcocite	Cu_2S	Metallic black-grey
Covellite	CuS	Submetallic blue
Cornetite	$Cu_3(PO_4)(OH)_3$	Greenish blue
Gerhardite	$Cu_2(NO_3)(OH)_3$	Translucent blue

Table 2.3 summarises some of the most common corrosion products, present in archaeological copper artefacts.

Bronze disease results from the presence of chlorides in the surrounding environment of copper which results in the formation of copper (I) chloride (nantokite). Nantokite is a grey waxy corrosion product that lies underneath other corrosion products, most of the time close to the metal core. Scott (1990: 193-206) reported the presence of nantokite in different parts of the metal. It can be adjacent to the original metal surface; above a cuprite layer and covered with other corrosion products such as malachite; replacing the metal core of a totally mineralised artefact; and in pits below the original surface of the object. In contact with water, nantokite reacts to produce basic copper chlorides (atacamite and/or paratacamite), resulting in the formation of pitting corrosion.

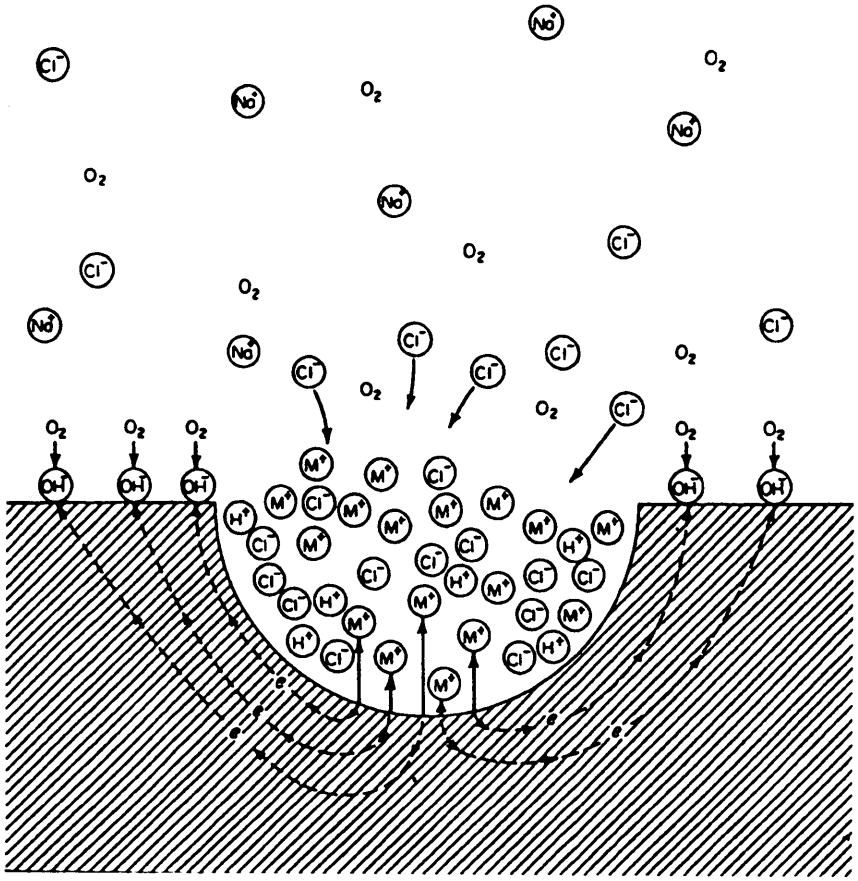


Figure 2.7 Pitting corrosion ***(after Fontana, 1987: 67).***

Organ (1963: 6) suggested that nantokite initially reacts with water to give cuprite and hydrochloric acid. The hydrochloric acid produced then reacts with copper to give new nantokite:

$$2CuCl + H_2O \rightleftarrows Cu_2O + 2HCl \quad (15)$$

$$2HCl + 2Cu + 1/2O_2 \rightarrow 2CuCl + H_2O \quad (16)$$

Scott (1990) published that nantokite reacts with water to give principally atacamatite or paratacamite:

$$4CuCl + O_2 + H_2O \rightarrow 2\ Cu_2(OH)_3Cl + H^+ + Cl^- \quad (17)$$

From the above-mentioned is clear that the presence of nantokite, consequently the presence of chlorides, accelerates the corrosion rate causing disruption of the original object form and appearance, and affects the acidity of the copper surface.

The nature and composition of corrosion products depends on the composition of the alloy. Corrosion of bronzes (copper-tin alloys) is often considered similar to that of pure copper. Analysis of bronzes has shown mainly copper corrosion products (such as cuprite, malachite, atacamite and brochantite depending if the objects were found in soil, sea or atmosphere) with tin being selectively corroded and removed (destannification). An exception to this is the presence of tin corrosion products in high tin bronzes. Similarly to copper, the corrosion of bronzes is dependent on the composition of the alloy and the environment they are exposed to. Robbiola *et al* (1998: 2083) analysed archaeological bronze objects and found 2 main types of pattern depending on whether the original surface boundaries are preserved (type I) or are damaged (type II). The composition of the

corrosion layers was relative to the composition of the soil, however, decuprification was observed in most cases with corrosion layers enriched in tin because of this copper dissolution.

The corrosion of brasses (copper-zinc alloys) is often characterized by selective dissolution of zinc (dezincification). Zinc corrodes leaving a weak, brittle and porous copper/copper oxide layer and can be uniform or localised (known as 'plug'). Brasses containing more than 30% zinc are more prone to dezincification. Dezincification takes place in two ways, either through selective corrosion of zinc or through corrosion of both copper and zinc and then redeposition of copper as the more noble metal (Scott, 2002: 27-28).

CHAPTER 3

3 Corrosion Inhibition of Metals

3.1 Corrosion Inhibition Mechanisms

There are several ways to retard corrosion of metals, the implications of which are not always known or ethically acceptable. Unlike in industry, where the corrosion of metals has large financial implications and corrosion protection systems are well advanced, in the conservation of archaeological and historical metals the options are limited and are far less well developed.

The main concern in the conservation of metals, especially when dealing with active corrosion, is to slow down the corrosion process. Methods such as washing to remove soluble chloride ions are time consuming and not always successful, whilst others such as electrochemical methods (as well as requiring a considerable input of time) cause chemical and physical changes, which may not be ethical. They also entail an expertise not always available amongst conservators. Corrosion inhibitors have been in use for a long time as they provide a cheaper, easier and faster way to retard corrosion without drastic alterations of existing patinas.

This chapter discusses the theory behind corrosion inhibition of metals, the function of different chemical groups that are used as inhibitors, the factors affecting their effectiveness, ways of classification and the synergistic effect between different compounds

that were used for this thesis. Following this, there is a review of compounds that have been used or tested in the field of conservation of archaeological objects to investigate their function on corroded metals. Special reference is given to benzotriazole as the most widely used inhibitor in conservation of archaeological copper and copper alloys as well as main subject of this thesis.

Finally, a literature review of the selected compounds tested in this thesis and the reasoning behind this concludes this chapter.

3.2 Definition of Corrosion inhibition

Although extensively used in conservation of copper and copper alloys, the exact mechanism of corrosion inhibition is not yet completely understood. There are many variables that have to be taken into account in order to explain the way inhibitors work. In general terms, inhibitors retard corrosion by affecting either the thermodynamics or the kinetics of the metal/electrolyte system. Sastri (1998: 33) supported the idea that inhibitors affect corrosion by increasing the overvoltage of the hydrogen ion discharge on the cathodic reaction of the corrosion process or the resistance of the inhibitor film at the metal/system interface. Corrosion inhibitors also retard the corrosion process by altering the kinetics of the electrochemical reactions. The reactions that take place between a metal and an inhibitor depend on the charge of the metal and the composition of the inhibitor as well as the environment (Rozenfeld, 1981: 3).

3.3 Corrosion inhibition mechanism

Corrosion takes place mainly through the anodic dissolution (oxidation) of a metal. Inhibitors retard the corrosion rate of the metal dissolution mainly by varying the reactions responsible for the dissolution. The introduction of the inhibitor on the metal surface results in a corrosion potential that is modified to more passive value. The electric double layer on the metal/electrolyte interface changes as well. The inhibitor molecules reach the inner Helmholtz plane and are bonded to the free metal ions and change the structure and the composition of the double layer. Whilst all inhibitors act to retard the overall corrosion process, their mode of action varies depending on the manner of their deposition, which in turn is affected by factors such as the pH of the solution in contact with the metal (Kuznetsov, 1996: 2-3, Sastri, 1998: 35).

It is generally accepted that in neutral solutions (pH around 7) the main mechanism of inhibition is that of film formation on the metal surface, whilst in acidic solutions (pH<7) the inhibition takes place through adsorption of the inhibitor on the surface.

Film forming inhibitors, are predominantly salts (e.g. zinc or calcium salts) that form insoluble compounds either by reaction with the metal surface, or by reaction within the solution, followed by precipitation on the surface. The result in this case is a film that functions as a physical barrier and hinders the diffusion of oxygen to the metal. These compounds act mainly as cathodic inhibitors. In the same division also belong anions of weak acids that stabilise the oxide layer on the metal producing a passive layer of metal oxide. These anions act as anodic inhibitors (Shreir *et al*, 1994: 17:47).

In acidic solutions, inhibitors are predominantly adsorbed on the metal. The charge of the metal, and the composition and structure of the inhibitor determine whether *physical adsorption* or *chemisorption* will take place. In physical adsorption, the inhibitor is bonded to the surface by electrostatic forces between the electrically charged metal and the inhibitor. The inhibitor molecules are not in contact with the metal ions, but with the water molecule dipoles on the electric double layer which cover the metal surface. Bonds formed by physisorption are generally weak, and reversible, as the inhibitive species could be desorbed relatively easy. In chemisorption, the inhibitor interacts directly with the metal, electrons are transferred and a co-ordinate bond is formed. Chemisorption takes place slowly in relation to the physisorption. Bonds resulting from chemisorption are stronger and cannot be completely reversible. From a general point of view, the composition of the metal or alloy and the composition of the inhibitor determine the bond that is formed and its strength (Sastri, 1998: 35-40).

Adsorption is affected either by the residual charge of the metal surface and the nature and chemical structure of the inhibitor, or by the nature of the metal. (Sastri, 1998: 36). In the case of physisorbed inhibitors, which are bonded electrostatically on the metal surface, their adsorption on the metal surface is mainly affected by the charge of the metal. Consequently, the degree of adsorption is not related to the composition of the metal, and so different metals with the same potential will have the same adsorption of a given inhibitor. This case excludes metals with impurities, which result in different values of surface charge and consequently different degrees of adsorption (Kuznetsov, 1996: 2). However, the degree of adsorption is closely related to the concentration of the inhibitor.

All the above-mentioned, explain the inhibition mechanism on clean metal surfaces, which are either free of oxides, or covered by thin air-formed oxides, (e.g. cuprous Cu_2O and cupric CuO oxides) where the inhibitor has access to the metal core. Archaeological copper artefacts have rarely "clean" or oxide-free surfaces. They are covered with complex corrosion products that involve compounds, such as nantokite, that accelerate corrosion. Inhibitors cannot have access to the metal when applied on the corrosion products, even if there is some metal core remaining. Unfortunately, little is known of inhibition mechanisms on corroded surfaces. Additional variables have to be taken into account in order to understand inhibition on archaeological metal artefacts. Surface condition and the composition of the corrosion layers have a very important influence on how inhibitors act. Corrosion products such as nantokite result in acidity of the metal surface. It has been suggested that inhibitors on corroded surfaces act either by adsorption, or by formation of a three-dimensional surface film, which act as a barrier that protects metal form the corrosive environment (Fiaud, 1995: 946, Turgoose and Duncan, 1992: 277, Weisser, 1987: 106).

3.4 Primary and Secondary Inhibition

The degree of inhibition can change over time, either as a result of surface reactions or the formation of the metal/inhibitor complexes. The inhibition that results from a reaction between the inhibitor and the metal is called *primary inhibition*. *Secondary inhibition* occurs at a later stage, is due to the reaction products of the primary inhibition, and typically takes place in acidic solutions. Depending on the nature of these products, secondary inhibition can be more or less effective than the initial (primary) inhibition, however it is frequently more effective (Wu, 1993: 14)

3.5 Factors that affect the effectiveness of inhibitors

The effectiveness of an inhibitor depends on many factors, including the composition of the metal and the inhibitor, the oxidation/reduction potential, the film that is formed and how adherent is to the metal, and the pH of the solution or of the metal/inhibitor interface. In addition, the inhibitor can also have a significant effect depending on factors such as the method of application, the concentration of the inhibitor, the time of immersion and the temperature of the solution in which the inhibition takes place.

The composition of the metal or alloy plays a very important role in the choice and effectiveness of inhibitors. Inhibitors therefore must be selected for each metal and environment individually. For instance, compounds that effectively retard the corrosion of one metal could cause accelerated corrosion of another metal. The latter could be a problem for objects that are composed of two or more different metals, such as gilded metal surfaces. Therefore the selection of inhibitor has to take into account the individual characteristics of each metal or metal alloy artefact.

The composition and molecular structure of each inhibitor are of primary importance, as they will affect the type and strength of the bond that is formed. For example, organic inhibitors that include multiple bonds or aromatic rings on their molecule will probably result in the formation of a strong co-ordinate bond between the metal and the inhibitor (Rozenfeld, 1981: 133). The composition of the inhibitor is of major concern in the conservation of archaeological copper. The inhibitive efficiency of an inhibitor that is applied on "clean" copper differs from the efficiency when applied on corroded copper. The

functional groups of the inhibitor maybe bonded with ions from the corrosion products (e.g. chloride ions), as they do not always have access to the metal.

Another factor that mediates the efficiency of the inhibitors is the chemical stability of the compounds used. This determines whether or not the initial inhibitor will form secondary products after the completion of the inhibition process, where the system is in equilibrium, and determines the rate at which these changes take place (Sastri, 1998: 162).

3.6 Factors affecting the function of inhibitors

As discussed above, the function of an inhibitor is closely related to the composition of the metal object to which it is applied. However the effectiveness of inhibition treatments is also mediated by other factors, such as: the concentration of the treatment solution; the presence of anions; pH and temperature. The concentration of a compound intended to inhibit corrosion is key for its effectiveness. Figures 3.1 and 3.2 illustrate the efficiency of corrosion inhibitors in relation to their concentration. The degree of inhibition and the corrosion rate decrease with higher concentrations of inhibitor. Inhibitors can be effective above a certain concentration, but when added in smaller concentrations they can also stimulate corrosion. This is due to the inhibitor only partially covering the surface, causing localised corrosion. Following this, the corrosion rate can be considerably greater than if no inhibitor were added (Putilova, *et al* 1960: 12).

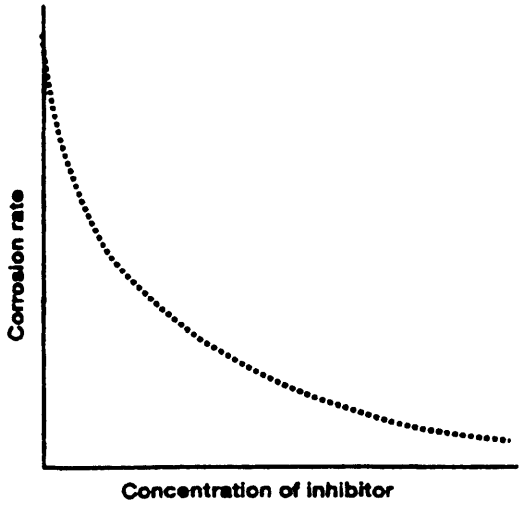


Figure 3.1. Corrosion rate of a metal in relation to the inhibitor concentration ***(after Sastri, 1998: 37).***

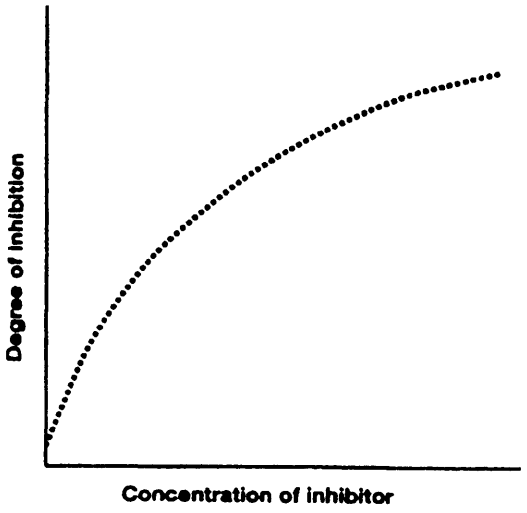


Figure 3.2. Inhibition efficiency in relation to the inhibitor concentration ***(after Sastri, 1998: 37).***

The presence of corrosion products on the metal surface governs the concentration of inhibitors required within the treatment solution. In general, metals covered with corrosion products, as is typically the case with archaeological copper and copper alloy artefacts, require higher concentrations of inhibitor, this is dependent on the nature and degree of the

corrosion (e.g. composition of oxides, porosity of corrosion layers). Faltermeier (1995: 162) suggested that in porous corrosion products, the inhibitor could deposit within the pores and act as a buffer material that could repair incidental damage of the polymer film afterwards.

In addition, the effectiveness of an inhibitor is also affected by the presence of anions such as chlorides or sulphates in the corrosive environment, as is often the case in buried archaeological artefacts. Consequently, the concentration of inhibitor required is proportional to that of these anions (Shreir *at al*, 1994: 17:15-16).

The pH of the solution, or that of the inhibitor/metal interface, also has to be taken into account as most inhibitors have an optimum pH range (Shreir *et al*, 1994, 17:17). Moreover the pH affects the polymerisation of the film and its thickness. For example, benzotriazole on copper works well at around pH 7, while it is less effective in more acidic conditions (below pH 4). In acidic solutions the Cu-BTA film grows fast and its polymerisation is not complete, which results in a thick film that is not effectively protective. Alternatively, in a around pH 7, the film grows slowly, is thinner, and highly protective (Brusic *et al*, 1991: 2253).

Temperature also affects the efficiency of inhibitors, as certain compounds perform better at higher temperatures (though these should not exceed 100°C). The temperature also affects adsorption of inhibitors. Physical adsorption is not dependent on the temperature, because of its low activation energy, whilst chemisorption is dependent. Therefore, the

inhibitive efficiency of inhibitors that are chemisorbed on the metal surface increases with temperature (Sastri, 1998: 39).

The inhibition process is also affected by the method of application. Immersion of an object under vacuum could enhance the adsorption of the inhibitor on the metal surface, and consequently inhibition, due to the removal of adsorbed oxygen. The time of immersion also influences the secondary inhibition that could take place over time, as a result of the by-products of the initial reactions. Partial vacuum has been used for BZA applications but has not been the subject of systematic study.

The efficiency of inhibitor compounds can be measured as follows (Skerry, 1985:5).

$$\mathbf{IE\% = [(CR - CR_i)/ CR] \times 100} \qquad (18)$$

Where:

IE: inhibitive efficiency,

CR: is the corrosion rate of metal without inhibitor, and

CR_i: the corrosion rate after the metal has been treated with inhibitor

The corrosion rate can be calculated in a number of ways, (e.g. as weight loss before and after inhibition, or the corrosion current i_{corr}), as long as both CR and CR_i are measured in the same system (Schweitzer, 1998: 131).

3.7 Classification of Corrosion Inhibitors

There are many ways of classifying inhibitors, for example; as passivators, precipitators, anodic, cathodic, mixed, organic, inorganic, vapour phase, absorbents, neutralising,

interface, safe, and dangerous, to name but a few. There are many different systems of classification, which define these compounds, according to the manner of their action (anodic, cathodic), their chemical nature (e.g. organic or inorganic), or the environment they are effective in (Skerry, 1985:7). For example Evans (1960) adopted a system based on the reaction mechanism being retarded and accordingly describes inhibitors as anodic, cathodic, or mixed. Sastri (1998:29) classified inhibitors into hard, soft and borderline. However, none of these classification systems are entirely satisfactory, and combined they do not form a complete whole. Moreover, the categories adopted are not mutually exclusive, and hence compounds can be classified in more than one class. Nevertheless, these classifications have provided a worthwhile contribution towards an understanding of inhibition processes. In view of this, some of the most important classes of inhibitors are discussed here in more detail.

3.7.1 Anodic inhibitors

Anodic inhibitors can be defined as chemical substances that, when added to a metal or a corrosive environment, affect the anodic reactions of the electrochemical process.

$$M \rightarrow M^{n+} + ne^{-} \text{ (anode)} \qquad (19)$$

Anodic inhibitors are amongst the most effective compounds for the prevention of metal corrosion. They reduce the corrosion rate, either by preventing the migration and dissolution of metal ions; raising the potential of the metal/metal oxide surface; or by forming passive films as a result of anodic dissolution (Rozenfeld, 1981: 79).

The potential-current diagram illustrates the effect of inhibitors on the anodic reactions. The introduction of the inhibitor provokes the polarisation of the anodic sites ($E_{corr} \rightarrow E_{c'}$). The potential increases ($i_{corr} \rightarrow i_{c'}$), causing a decrease in the corrosion current, which results on the inhibition of corrosion (Skerry, 1985: 9).

Anodic inhibitors can be further subdivided into oxidising and non-oxidising inhibitors. Oxidising inhibitors retard anodic reactions even in the absence of oxygen, whilst non-oxidising inhibitors act only when oxygen is present. In general, higher concentrations of non-oxidising inhibitors are needed in order to have a positive effect. They react with the metal ions to form thick protective films, and probably help to increase the chemisorption of dissolved oxygen onto the metal (Jones, 1996: 506).

Unfortunately, when the concentration of an anodic inhibitor is insufficient, only part of the metal surface is covered with the inhibitor. The regions of the surface covered with inhibitor act as anodes, whilst the uncovered surface acts as a cathode. This results in localised corrosion which eventually causes accelerated corrosion. In this case the corrosion rate is greater than the rate of the corrosion of the untreated metal. Consequently, these inhibitors have been called 'dangerous' (Evans, 1960: 199).

3.7.2 Cathodic inhibitors

Cathodic inhibitors affect the cathodic electrochemical process by retarding the cathodic reaction. They affect different stages of the cathodic process, such as the diffusion of

oxygen to the metal surface and the discharge of hydrogen (H^+) as well as changing the corrosion potential (Rozenfeld, 1981: 85). As stated previously, the exact nature of the cathodic reaction is dependent upon the pH of the electrolyte solution:

$$O_{2(aq)} + 2H_2O + 4e^- \rightarrow 4OH^-_{(aq)} \quad (20)$$

Whereas in acidic solutions hydronium ions (H^+) are reduced:

$$2H^+ + 2e^- \rightarrow H_2 \quad (21)$$

This reaction could be written as

$$H^+ + e^- \rightarrow H \quad (22)$$

$$2H \rightarrow H_2 \quad (23)$$

In neutral solutions (reaction 20), cathodic inhibitors react with the hydroxide ion (OH^-) to form insoluble salts, which precipitate on the metal surface and block the diffusion of oxygen. In acidic solutions inhibitors mainly block the second reaction (21) of the hydrogen evolution (Jones, 1996: 506). Importantly, cathodic inhibitors only require contact with cathodic areas, and not with the metal, so it is possible for them to work on corroded surfaces which represent an advantage for the treatment of archaeological artefacts.

Figure 3.3 illustrates the potential- current diagram of a metal that undergoes cathodic inhibition. Cathodic inhibitors by affecting the cathodic reaction, cause decrease in the corrosion current ($i_{corr} \rightarrow i_{c'}$) that results on an decrease of the corrosion potential ($E_{corr} \rightarrow E_{c'}$) (Skerry, 1985: 8).

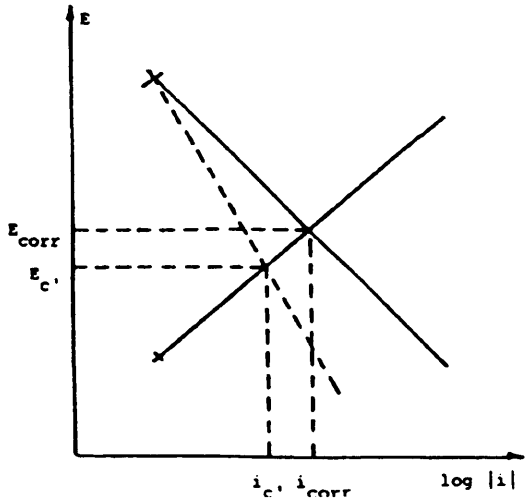


Figure 3.3. Potential-current diagram, of cathodic polarisation, induced by cathodic inhibitor *(Skerry, 1985: 8).*

Also cathodic inhibitors do not carry the risk of accelerating corrosion rate as anodic inhibitors do. Even if the concentration is insufficient, some corrosion layer will still be formed on the metal surface. The corrosion rate will not be greater than what it would have been without the inhibitor addition. These inhibitors are also known as 'safe' inhibitors. Consequently, even though cathodic inhibitors are not generally as effective as anodic they are used because they are often capable of retarding the corrosion rate in any concentration.

3.7.3 Organic and Inorganic inhibitors

This classification is based on the chemical nature of the inhibitor compound. The modes of action of organic and inorganic inhibitors are significantly different. Inorganic inhibitors are predominantly used in neutral media and affect mainly the anodic reactions. Their function is closely related to passivation. Organic inhibitors are used in acid media and primarily alter the cathodic reaction.

Inorganic inhibitors function by adjusting the pH to more alkaline levels, or by forming insoluble compounds on the metal surface. Common inorganic inhibitors are chromate and nitrite compounds. However, they are not widely used because of their toxicity and adverse effect on the environment. Recently chromates have been replaced by more environmentally friendly tungstates or molybdates (Sastri, 1998: 29).

Organic compounds containing sulphur or nitrogen and other elements from Groups V and VI of the periodic table are also used as corrosion inhibitors. These organic compounds are adsorbed onto the metal, either by physisorption or chemisorption. In general compounds that contain sulphur are better inhibitors than those that contain nitrogen or oxygen.

The effectiveness of organic compounds depends on many factors, such as the size of the organic molecule, the length of the chain, the number of atoms or groups that are bonded with the metal, and their ability to form continuous and compact films. For example long hydrocarbon chains are adsorbed on more strongly due to Van der Waals forces (Riggs, 1981: 12, Sastri, 1998: 41).

In the conservation of archaeological artefacts, organic inhibitors, such as benzotriazole or amines, are in use. Inorganic inhibitors should be avoided, as they could cause chemical modifications of the metal surface. The presence of inorganic compounds could also affect future analysis of the metal artefact.

3.7.4 Interface and Interphase inhibitors

Interface inhibitors are inhibitors that react directly with the metal surface. Interphase inhibitors are defined as inhibitors which react with the corrosion layers that cover the metal. The properties of the film that is formed depend on the interaction between the inhibitor and the metal (Craig, 1991: 90-91, Lorenz and Mansfeld, 1986: 467)

In the interface inhibition a two-dimensional film is formed by adsorption of the inhibitor on the bare metal. The adsorption in this case depends on the potential of the metal. The interface inhibition takes place in three different ways. The first is referred as geometrical blocking. The surface is covered with the inhibitor, which acts as a physical barrier. The degree of inhibition depends on the degree of the surface coverage. The second type is the deactivating coverage, where the inhibitor reacts only with the active (anodic) parts of the surface. As a result of this, the inhibitor impedes the corrosion reactions. The reactions that are restrained may be anodic, cathodic, or both. The third type is the reactive coverage, where the inhibitor takes part in the corrosion reactions to reduce the corrosion rate. The inhibitive effectiveness is proportional to the degree of coverage of the metal with the inhibitor. Interface inhibitors are less effective when metals are covered with corrosion products, as they have less access to the metal surface (Craig, 1991: 90-91).

Interphase inhibitors are often referred as passivators, as well as oxidising inhibitors. The interphase inhibition is related to the formation of a thicker three-dimensional film on the

metal surface. The inhibition effectiveness depends on the porosity, the stability, and the thickness of the film, as well as the time of immersion (secondary inhibition). Interphase inhibitors are more effective than interface for metals that are covered with corrosion products. They co-operate with the corrosion products to the formation of a protective film on the surface (Lorenz and Mansfeld, 1986: 467).

3.7.5 Vapour-phase

Vapour-phase corrosion inhibitors can be classified as the chemical compounds that within low pressure (10^{-2} - 10^{-7} mm Hg) can volatilise and protect a metal in an enclosed space (Jones, 1996: 510). VPI (Vapour Phase Inhibitors) or VCI (Volatile Corrosion Inhibitors) are used mainly in packaging, transportation, or display of artefacts. One of the main advantages that they have is that they could reach metal underneath the corrosion products, reaching gaps, or crevices (Skerry, 1985: 11). Organic molecules such as amine nitrate, carboxylates, and carbonates have been used as vapour phase inhibitors.

The mechanism of their function is considered to relate to the formation of an adsorbed film on the metal surface (Uhlig and Revie, 1985: 275). The protection that these inhibitors offer is temporary because the bonds between the metal and the inhibitor are weak. They can effectively retard the corrosion of a metal, as long as they are in a sufficient concentration, and in a sealed place. They have to diffuse on the metal fast, forming a stable environment for a sufficient period of time, for example one or two years (Scheifler, 1985: 36).

There are drawbacks in their use, such as their toxicity and the fact that they could accelerate corrosion of some non-ferrous metals when they are used to protect more than one metal. Their use in artefacts that consist of two or more metals has to be carefully considered. Moreover they have to be in a very well sealed space otherwise the vapours could escape, resulting in the initiation of corrosion.

Vapour phase corrosion inhibitors have been used in museum display cases, and for packaging in storage. For packaging, the artefacts are wrapped in paper impregnated with the inhibitor and placed in sealed polyethylene boxes. Benzotriazole has been used as a volatile inhibitor for packaging of copper and copper alloy artefacts. These inhibitors should not be used in combination with silica gel, as the gel absorbs not only water vapours but also vapours in general, including vapour inhibitors.

3.7.6 Hard, Soft and Borderline Inhibitors

Sastri (1998) suggested the classification of inhibitors as hard, soft and borderline. This is based on the hard and soft acid base theory (HSAB), by which hard acids react easier with hard bases, and soft acids react better with soft bases, whilst borderline compounds react with both. All chemical compounds and metals can be classified according to this theory into hard, soft or borderline acids, or bases. Copper(II) Cu^{2+} for example is classified as borderline acid that will react with borderline inhibitors, such as amines, whilst copper(I), Cu^{+} is a soft acid that could effectively inhibited by mercaptobenzothiazole which is a soft inhibitor. This classification could be a very useful tool for improving the understanding of

inhibiting reactions between metals and chemical compounds that are used as corrosion inhibitors. It could also help in the design of new inhibitors on a more scientific basis.

3.8 Synergistic Effect

In industry, it is common practice to combine more than one chemical compound to retard the corrosion process of a metal or alloy. This combined action of inhibitors is leading to better inhibition of the treated artefact. When two or more corrosion inhibitors are added to a corrosive environment of a metal or an alloy, the inhibition efficiency of the mixture may be greater than the sum of each one of the additives. This is called the synergistic effect (Rozenfeld, 1981: 110).

There are obvious benefits of the use of the synergistic effect for the corrosion inhibition for archaeological metals. Most of the times, the additives alone are not very effective inhibitors, but when combined together they present very good inhibitive properties. Different inhibitive features could be utilised, such as the combination of anodic and cathodic inhibitors together, which results in the retardation of both anodic and cathodic reactions of the electrochemical process.

The exact mechanisms of the synergism of inhibitors are not always exactly known. It has been suggested that some additives (e.g. halides) modify the surface features of a metal, increasing the adsorption of the inhibitor. An example of the aforementioned could be the synergism that halide anions (Cl^-, Br^-, and I^-) provide in the corrosion inhibition of iron. Kuznetsov (1996: 40) reported that halides alter the properties of the surface, making

possible the adsorption of organic cations onto the metal surface. The main area of the PhD research is the modification of BTA with other selected inhibitor compounds making use of the synergistic effect that has been reported to exist between BTA and certain compounds.

3.9 Inhibitors: A Review of Archaeological Applications

3.9.1 Introduction

Even though in industry there are many chemical compounds that are used as corrosion inhibitors for copper, in the conservation of archaeological copper artefacts, only a few have been tested and even fewer are in use. Benzotriazole is extensively used to stabilise bronze disease in copper. Other inhibitors that have been suggested are 5-Amino-2 Mercapto-1, 3, 4-Thiadiazole (AMT) and 2-Mercaptobenzothiazole (MBT).

The use of inhibitors for archaeological artefacts needs to take into account additional ethical and aesthetic considerations. Therefore, not all of the industrially effective inhibitors can be considered as suitable for archaeological use. In this section only the inhibitors that are in use or have been tested in conservation will be discussed.

The research in conservation of archaeological copper artefacts focuses on the testing procedure of the inhibitors. Inhibitors in industry are tested on clean or oxide free metal surfaces, which is not the case in archaeological objects. Most of the materials testing in the past was done on original archaeological copper artefacts. Angelucci *et al* (1978) produced an experimental procedure to test inhibitors on artificially corroded coupons. Faltermeier (1995) developed a more reproducible method to test corrosion inhibitors for the conservation of copper artefacts. The main concern of both was to develop a testing

procedure for inhibitors, which could be reliable, and reproducible. Archaeological artefacts are covered with different corrosion products, and can give highly variable results. Furthermore, archaeological artefacts because of their great significance and importance should not be used for testing as the accelerated corrosion tests could damage them. The aim of their studies was to develop artificially corroded copper coupons, which can represent archaeological copper corrosion products. On this basis, only a small selection of inhibitor combinations has been tested.

3.9.2 Benzotriazole

Benzotriazole ($C_6H_5N_3$) is a nitrogen-containing organic heterocyclic compound with structural formula:

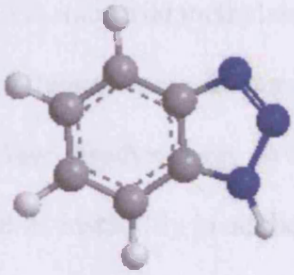


Figure 3.4. Benzotriazole molecule.

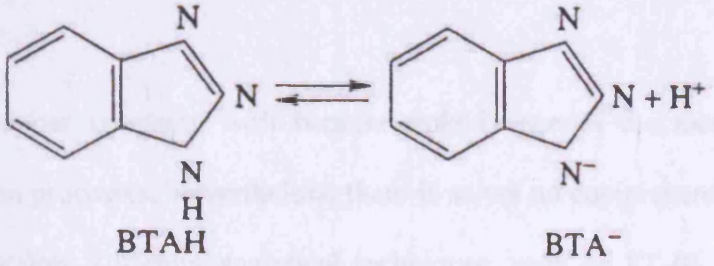


Figure 3.5. BTAH and BTA^- (*after Sastri: 1998: 868).*

Benzotriazole bonds with the copper surface, through the nitrogen of the triazole anion. In neutral solutions, both forms of BTA (BTAH and BTA^-) exist. The percentage of BTA^- increases with the increase of the pH and it is adsorbed easier than BTAH on copper (Sastri, 1998: 868-871). Xu *et al* (1993: 1000) suggested that a film of BTA^- is formed on the copper oxide surfaces when low concentration solutions are used for short times and that BTAH might undergo dissociation to BTA^- and H^+ during adsorption on the copper surfaces covered with oxides.

BTA is the most widely used inhibitor nowadays for the stabilisation of copper and copper alloys. Most articles cite Madsen (1967: 163-166) as the first propose the use of BTA for the conservation of archaeological artefacts. He used 3% by weight solution of benzotriazole in industrial methylated spirits (IMS) to treat bronze objects, with satisfactory results. The artefacts were immersed into the solution and a vacuum was then applied. Although a few disadvantages have been mentioned about the use of BTA, such as its volatility and its instability in acidic conditions, Madsen overcame these problems with the use of a lacquer (Incralac) applied over the BTA layer. Since then BTA has been widely accepted and used routinely.

The inhibition of copper corrosion with benzotriazole is one of the most thoroughly investigated inhibition processes. Nevertheless, there is as yet no comprehensive theory on its exact mode of action. Different analytical techniques, such as FT-IR, XPS, SERS,

SIMS, and electrochemical measurements[1], have been used to examine the copper/BTA complex, and understand its formation and its protective action. Dugdale and Cotton (1963) suggested that benzotriazole is predominantly a cathodic inhibitor, subsequently confirmed by Fox *et al* (1979). Fiaud (1995: 938) found that benzotriazole acts mainly as an anodic inhibitor, even though oxygen reduction is also retarded. He found that during inhibition both of the electrochemical reactions are kinetically controlled.

There are many theories on the mechanisms of the BTA's film formation, some of which are controversial. Cotton and Scholes (1967: 1-5) supported the formation of a two-dimensional polymeric film of copper-benzotriazole complex, which is chemically bonded on the metal/metal oxide surface. The thickness of the film was found to be less than 50 Å. The film includes both Copper(I) and Copper(II) ions. The stoichiometric ratio, by which BTA and cuprous compounds are bonded, is said to be 1:1. The structure of the polymeric formation of BTA cuprous complex ($C_6H_5N_3Cu$) is shown in Figure 3.6a. BTA forms complexes with cupric compounds in a ratio of 2:1. These complexes include anions, such as chlorides, oxygen, water, or hydroxyl groups that are essential for the stabilisation of the film. The suggested polymeric structure of BTA cupric complex is shown in Figure 3.6b.

Mansfeld *et al* (1971: 293) proposed that BTA is chemisorbed onto the metal surface and the film that is formed mainly prevents the adsorption of oxygen and slows down, or even stop the initial corrosion reaction of copper: $2Cu + O_2 \leftrightharpoons CuO_2$.

[1] FTIR: Fourrier Transformed Infra-Red Spectrometry, XPS: X-Ray Photoelectron Spectroscopy, SERS: Surface Enhanced Raman Spectroscopy, SIMS: Secondary Ion Mass Spectroscopy.

Poling (1970: 359-370) suggested that BTA is physically adsorbed on the surface and reacts with copper ions to give insoluble compounds that precipitate on the metal surface. Copper is bonded to BTA through the amino nitrogen. The polymeric film acts as a physical barrier. The film can be quite thick, up to several thousand Å (1 Å = 0.1nm). The colour of the Cu(I)BTA complex was described yellow to green. Poling also studied the chemical properties of BTA and Cu(I)BTA complex. An interesting note is that a small percentage of chlorides appear to remain in the complex, although its exact role and whether it is incorporated in the complex was not examined.

The composition of the copper oxide that covers the surface plays a very important role on BTA film formation. Roberts (1974: 289) showed that benzotriazole is adsorbed faster on Cu_2O surface than on CuO. On CuO benzotriazole bonds with both Cu^+ and Cu^{2+} to give Cu(I)BTA and Cu(II)BTA complexes. The Cu(II)BTA complex increases over time, due to further oxidation of Cu(I). The thickness of the film is relatively thin, at 7±3 Å. He also suggested that the polymeric structure of copper/BTA based on the bond length considerations was not the same as suggested by Cotton (Figures 3.6 b, c) because an overlapping of the benzene rings of benzotriazole can take place.

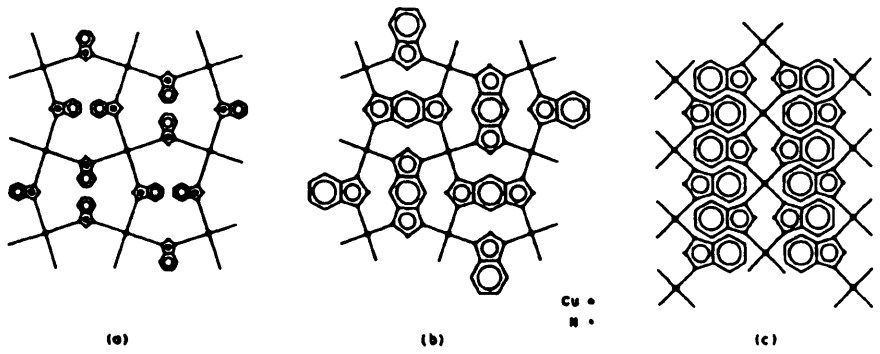


Figure 3.6. a-c: Polymeric structure of the Cu-BTA complex (after Sease, 1978: 80). (Figure a & b originally after Cotton and Scholes 1967, and Figure c after Roberts 1974)

The composition of the Cu-BTA complex has been the subject of many studies. Although in most cases studies agree that BTA is preferable bonded to Cu(I) surface, analysis has shown the presence of Cu(II). According to Chadwick and Hashemi (1978: 39) Cu(I)BTA is formed in solution which then is partly oxidised to Cu(II)BTA after exposure to air during the drying process. The length of time copper stays immersed into the BTA solution does not seem to have an effect on the Cu(II)BTA complex. The longer the treated surface stays exposed to air, the more oxidation of Cu(I) to Cu(II)-BTA occurs. The presence of cuprite on the copper surface leads to better adsorption of BTA. The thickness of the Cu(I)BTA film depends on the stability of the oxide layer. A thin Cu(I)BTA film is formed on a stable oxide layer (Chadwick and Hashemi, 1978: 39-51).

Other studies have examined also not only the way BTA bonds with metallic copper but also with copper oxide. Jiang *et al* (2004) investigated the way BTA bonds with cuprous oxide and suggested that BTA is chemisorbed into the Cu_2O surface through N3 and N2. The chemisorption of BTA on the copper oxide is a result of a chemical bond between

copper and the sp^2 nitrogen lone pairs as well as a hydrogen bond that takes place between BTA's N-H or C-H protons and the oxygen anion of cuprite (Jiang *et al*, 2004:12851-7).

Another model of the way BTA is bonded to copper is that developed by Fang *et al* (1986: 476). Fang *et al* suggested that BTA- "bridges" two copper ions through the two neighbouring nitrogen of the triazole ring. This way all the copper ions are linked into copper-BTA chains leaving no free atoms to corrode.

Brostoff (1997: 99-108) investigated the interactions of BTA formed on several copper corrosion products such as copper oxides, cuprite (Cu_2O) and tenorite (CuO), nantokite (CuCl), $CuCl_2$, paratacamite $Cu_2(OH)_3Cl$), malachite ($Cu_2(OH)CO_3$) and copper powders. This study also looked at how factors such as BTA concentration, pH of solution and solvent affect these reactions. The results showed that the CuBTA films formed were mixtures of more than one complex or phase with differences compositions, thickness and degrees of polymerisation. Side reactions were found to be of great significance for the process as they could result in inhomogeneous films. The proposed mechanism of Cu-BTA film formation in aqueous solutions was that of dissolution-precipitation resulting in decreased protection.

The pH of the solution plays a very important role in the film formation and the effectiveness of benzotriazole for copper inhibition. The film that is formed is dependent on the surface of copper (covered or not with oxides, and their nature) and the pH of the solution. Brusic *et al* (1991: 2253) reported that the BTA increased the corrosion potential,

retarding the corrosion rate of copper. This implies that benzotriazole primarily blocks the exodus of copper ions and acts as a barrier to oxygen diffusion. The kinetics of the film formation, its thickness and the degree of polymerisation depend on the pH of the solution. In very acidic solutions (pH<2) a thick film (up to 25 nm) grows quickly. This follows a dissolution-precipitation mechanism, and as such the polymerisation is not complete. Therefore, although the film is thick, it is not very protective. At a pH of around 7, the film grows more slowly in a self-inhibiting manner. It is thinner (0.5-4 nm) and is completely polymerised providing the best protection. Therefore the degree of protection is found to be proportional to the degree of polymerisation. Finally different oxides give different films, and the structure of the film is dependent on the copper oxides.

Musiani *et al* (1987: 201) using electrochemical and SERS techniques also found that the inhibitive efficiency of BTA is pH dependent. Its adsorption on copper is weakened at low pH values. They showed that the adsorption of aggressive anions, such as chlorides is increased in acidic BTA solutions, which may be responsible for the drop in effectiveness.

Benzotriazole has many industrial applications such as dyestuff, optical brightener, photostabiliser as well as corrosion inhibition of metals (Bigotto *et al*, 1996: 511). Magaino *et al* (1998: 217) suggested that BTA as a pre-treatment for polyurethane paints for the protection of outdoor copper inhibited not only copper corrosion but also acted as a stabiliser for the paint.

Although the action of BTA on copper is more or less studied and known, its effect on other metals present on copper alloys, such as those with tin or zinc, is yet to be established. BTA has been studied and used as a corrosion inhibitor for zinc, silver, cadmium, aluminium and iron. Ammelloot *et al* (1999: 2549-2558) suggested that although BTA inhibits copper corrosion it does not have any effect on tin corrosion. However, analysing pure copper and bronze surfaces with and without the presence of BTA they found that the behaviour of bronze is similar to that of pure copper. Chadwick and Hashemi (1978: 39-51) examined copper-zinc alloys and found that zinc forms a complex with BTA, the exact mechanism and composition of which is not known.

It is known that BTA often fails to stabilise copper or copper alloy archaeological artefacts. One explanation for this could be that archaeological artefacts are covered with thick corrosion layers that hinder the inhibitor's access to the metal surface. The corrosion products often include anions such as chlorides that hinder the inhibition process. These anions contribute to a low pH (<3.5) on the metal surface. As has already been mentioned, in acidic pH values, the film that is formed is not completely polymerised, and therefore is less effective.

In conclusion, many factors seem to affect the copper-BTA complex formed and its properties, consequently the effectiveness of the BTA. These include the copper surface the BTA is applied to and whether or not it is covered with copper oxides or other copper compounds, the presence of aggressive anions in the environment (e.g. chlorides), the amount of oxygen present, the pH of the solution, the potential of the metal that is treated

and also the temperature. All these factors are often interrelated, however their relationships are not always clear. The different theories regarding the BTA mode of action may be a result of the interactions taking place between different factors such as those above-mentioned, during experimental or analytical conditions. Moreover, in the conservation field research is more limited with many unanswered questions due to the complexity of the archaeological material compositions and variable environmental conditions.

3.9.3 2-Amino-5-Mercapto-1, 3, 4- Thiadiazole (AMT)

2-amino-5-mercapto-1, 3, 4- thiadiazole ($C_2H_3N_3S_2$) is a heterocyclic compound. Its molecular structure is illustrated in Figure 3.7.

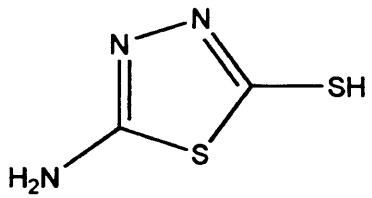


Figure 3.7. Molecular structure of 2-amino-5-mercapto-1, 3, 4- thiadiazole.

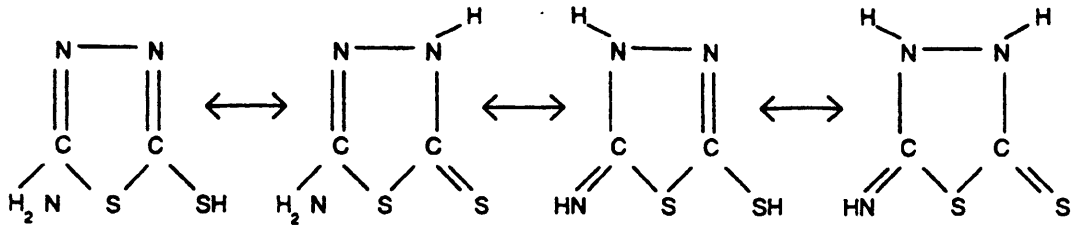
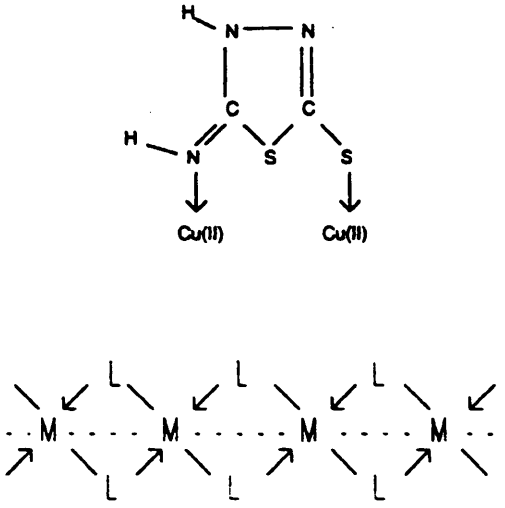


Figure 3.8. Tautomeric forms of 2-amino-5-mercapto-1, 3, 4- thiadiazole (after Gajendragad and Agrawala, 1975: 1331).

AMT is soluble in both water and organic solvents. It has four tautomeric forms (Fig. 3.8). In contact with copper, AMT forms an insoluble polymeric film with copper ions.

Gajendragad and Agrawala (1975) suggested that AMT bonds with copper in the following structure (fig 3.9):



M = Cu(II), L = structure above

Figure 3.9. Copper-AMT structural bonding ***(after Gajendragad and Agrawala, 1975)***

2-amino-5-mercapto-1, 3, 4- thiadiazole was first tested by Ganorkar *et al* (1988: 97-101) for the stabilisation of copper archaeological artefacts. Corroded copper alloy coins were treated with AMT, 0.01 M aqueous solution. The coins were first washed several times to remove soluble salts (e.g. chlorides). They were then immersed into the inhibitor solution with a few drops of nitric acid (1:1) to accelerate the reaction, and heated to 60°C under vacuum. After the immersion, a yellow-green precipitate was observed and the treatment repeated until no precipitate was viewed. After the AMT treatment the artefacts were washed with distilled water and dried. The treatment was reviewed as satisfactory, compared to the BTA treatment.

Ganorkar *et al* (1988: 97-101) supported the idea that AMT first reacts with the copper chloride on the metal surface, dissolving all the chlorides from the corrosion products. When all the chlorides are removed, a thin polymeric layer is formed, which covers the surface. The results have been confirmed with IR reflectance studies. The copper ions mainly bond with the sulphur.

Uminski and Guidetti (1995: 274-278) tested AMT as a reagent to remove chloride ions from artificially corroded bronze plates. They reported that AMT does not function well as a reagent to dissolve copper chloride. They also stated that treated coupons are often discoloured. After the treatment, the bronze plates appeared to be grey-green with brown spots. This is in direct contrast to the Ganorkar *et al* (1988) results.

Faltermeier (1995: 285) tested AMT on artificially corroded copper coupons and on archaeological copper alloy artefacts. He found that its inhibitive efficiency varied in different values of relative humidity. AMT was more protective than BTA, when tested for 24 and 48 hours at 95% relative humidity but it was less effective than BTA in long-term tests at similar RH values and could not offer a satisfactory degree of protection when tested in extreme values of relative humidity ($RH \simeq 95 \pm 5\%$). One of the main disadvantages that he reported was the colour change to the copper surface after AMT treatment. Copper coupons appeared to be brown-yellow. It also caused colour changes to nantokite, malachite and cuprite. The discoloration was greater in higher concentrations and for immersion longer than 24 hours. Repeated treatments have to take place (Faltermeier, 1995:285-288).

Hawley (1996: 77) treated a large number of bronze objects with AMT as a means of extracting chlorides. The method was found effective with one main drawback reported the removal of "sludge" from the difficult areas (i.e. crevices).

Mohamed *et al* (2004: 369) also examined the performance of AMT for use in conservation. The copper coupons were immersed into 0.01M AMT in methanol for six hours. The coupons were exposed to the museum environment for five years. Weight change measurements and FTIR were employed for inhibitive efficiency assessment and characterization of the complex formed. AMT was found to be less effective than BTA in both monitoring intervals (six months and five years). The FTIR analysis showed that AMT is bonded to copper through both the sulphur and nitrogen of the molecule.

AMT has been also tested for industrial purposes. It has been found that it is bonded to copper through the nitrogen of its molecule, forming an insoluble complex that results in shifting of the corrosion potential into more positive values (Zucchi *et al*, 1996:153).

Otero and Bastidas examined the efficiency of BTA and AMT in 5% citric acid solutions for the cleaning of copper alloys. The two compounds were reported as anodic inhibitors of similar efficiency (Otero and Bastidas, 1996:133-138). Bastidas and Otero (1996: 333) tested the efficiency of AMT and BTA in hydrochloric, sulphuric and citric acid. AMT was found to be more effective in the former two acids, whilst in the latter acid its efficiency was similar to BTA. Interestingly, AMT has been reported to act as a cathodic inhibitor in a

citric acid solution, anodic in sulphuric acid and cathodic in hydrochloric acid. Consequently, the effect of AMT on the anodic or cathodic reactions seems to be subject to the solution and these conditions govern the reaction.

One of the main drawbacks of the use of AMT is its toxicity. AMT causes irritation to skin and could be harmful if inhaled, as it produces toxic fumes of carbon monoxide and carbon dioxide (Aldrich, safety data sheet, 1999). AMT is also moisture sensitive, which makes it more difficult to work with. It should always be stored under a nitrogen atmosphere, however this is not always available in conservation laboratories.

3.9.4 Mercaptobenzothiadazole (MBT)

Mercaptobenzothiadazole ($C_7H_5NS_2$), is a sulphur-containing heterocyclic compound. Its molecular structure is illustrated in Figure 3.10.

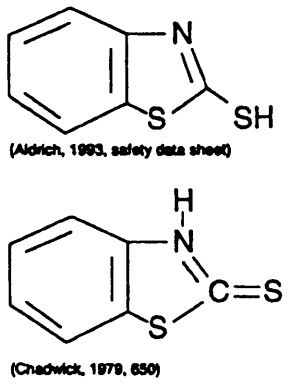


Figure 3.10. Molecular structure of mercaptobenzothiadazole {Faltermeier 1995: 69}.

MBT is considered to be the most effective of the mercapto compounds as an inhibitor for copper. Its efficiency increases with an increase in concentration. Nevertheless it is only slightly soluble in water. It forms a complex with copper, mainly with copper(I) ions

through the nitrogen atom. The thickness of the Cu-MBT complex varies, and is dependent on the concentration. The film that is formed at higher concentrations is thinner and more protective (Faltermeier, 1995: 71).

Musiani *et al* (1987: 191) found that the inhibitive efficiency of MBT equals that of BTA in alkaline solutions, whilst in more acidic solutions (e.g. pH≃2) the inhibitive efficiency of MBT is reported to be 95% whilst that of BTA is 60%. This supported the view that MBT (unlike BTA) is an effective corrosion inhibitor in a wide range of pH values. The latter makes MBT a possible corrosion inhibitor for copper and copper corroded artefacts that suffer accelarated corrosion as the pH of the pits of bronze disease is reported to be 3 or lower (Drayman-Weisser, 1987: 107).

Faltermeier (1995: 283-285) reported that MBT retards corrosion effectively (inhibitive efficiency 95%). In comparison with AMT and BTA, MBT was by far more effective. Unfortunately,. Faltermeier reported that MBT affects the colour of the artefacts discolouring the copper surface, causing a yellowing of the overall apearence. This alone makes it unsuitable for use in archaeological artefacts.

Mohamed *et al* (2004 : 376) tested MBT in long term exposure to museum conditions and found that MBT, although forming a complex with copper I was not effective in the testing conditions after six months.

The most important disadvantage of MBT is its toxicity and possible carcinogenic properties. It produces toxic fumes of carbon monoxide, carbon dioxide, as well suphur and nitrogen oxides. Precautions have to be always taken for its use in a conservation laboratories (Aldrich, Safety Data Sheet, 1999).

3.9.5 Health and Safety Considerations

In recent years there has been an increased concern about the toxicity of materials used in conservation. In industry controlled testing is currently taking place on organisms of different trophic levels to establish the degree of toxicity of the compounds used as inhibitors (Sastri, 1998:886-887).

The disposal of inhibitive compounds is of great importance, as certain compounds such as chromates cause serious environmental problems (Shreir *et al*, 1994: 17:19). Low toxicity inhibitors have been tested in industry in the hope of replacing toxic compounds (Stupnišek-Lisak *et al*, 1998: 713).

In conservation of antiquities great awareness has grown regarding the use of benzotriazole, the most widely used inhibitor. Oddy (1972: 135, 1974: 188) mentioned the 'uncertain' toxicity of benzotriazole, and the necessity for further investigation of this issue. However, despite numerous calls for more research the question still remains as to the exact nature of the health threat and furthermore this is clearly beyond the scope of the conservation field. In general terms, many precautions have to be taken during use of BTA. Compounds like MBT, that are possibly carcinogenic and toxic, have to be used only in laboratories with

appropriate equipment (e.g. fume cupboards and personal protective equipment) in order that the user is protected. Care in preparation and disposal of such materials is of great importance in a conservation laboratory and all the precautionary statements of the materials used have to be taken seriously into account.

In the recent years research is undertaken on methods to abate toxic materials to levels that could be acceptable for the environment. One of these methods involves advanced oxidation processes (AOP) which make use of strong oxidants such as O_3 and H_2O_2 applied with the help of UV devices and catalysts to promote the reactions. A method that has been used for BTA is that of photochemical oxidation using H_2O_2 and UV. The method is reported to be promising for both small and large scale applications (Andreozzi *et al*, 1998: 93-98).

3.10 Selected inhibitive compounds

A literature survey was undertaken with the aim to find combinations of compounds that could be used potentially as inhibitors in conservation of archaeological copper and copper alloys artefacts. One of the main objectives was to use compounds that are actually more effective than BTA alone for the stabilisation of active corrosion. For this reason, compounds used in chloride-containing environments were examined. Compounds, effective in acidic conditions (e.g. HCl, H_2SO_4 solutions) were also considered.

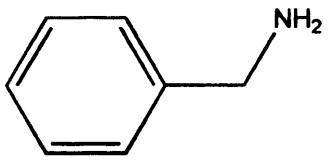
The survey of eco-friendly compounds (e.g. methyl-imidazole) and some initial laboratory tests lead to quick testing and exclusion of some compounds for several reasons. However, one of the compounds presented as eco-friendly exhibited the same health and safety risks

as BTA. Some of the compounds were excluded as very toxic compounds (e.g. mercaptobenzothiazole). Another reason for the exclusion of certain compounds was the colour changed observed during the treatments.

For this survey the use of the synergistic effects of certain compounds with BTA was selected to be investigated in depth because of the possibilities offered. Six compounds were selected, only one of which has been tested and partially used in conservation as a single compound, not in combination with BTA. This is 2-amino-5-mercapto-1, 3, 4-thiadiazole (AMT), the theory of which was presented earlier in this chapter. The other five compounds are presented below in alphabetical order.

3.10.1 Benzylamine (C_7H_9N)

Benzylamine (BZA), although not an inhibitor when used on its own, has been added in BTA solutions in order to improve the overall effectiveness in chloride-containing environments. BZA is a primary aromatic amine (containing NH2 group in its molecule) and benzyl ($C_6H_5CH_2$) describes the other functional group in the molecule. The molecule of BZA is given in figure3.11. Benzymanine is also known as monobenzylamine, benzenemethanamine, alpha-Aminotoluene, (Phenylmethyl)amine, and Aminotoluene.



benzylamine

Figure 3.11. Molecular structure of benzylamine (BZA).

Fleischmann *et al* (1983: 1325-1333) tested the effectiveness of the combination by both simple immersion and in combination with anodization and found that the presence of BZA did improve the overall corrosion protection provided by BTA when applied with anodization. The synergistic effect between the two compounds was attributed to the formation of a cupric-BTA complex which appeared to be thermally more stable than the cuprous complex. The addition of BZA aided the formation of this complex by causing a shift in the potential that lead to the formation of a cupric complex because of the greater affinity of BZA towards cupric ions.

Another study by Fleischmann *et al* (1985: 1591-1602) showed that the addition of BZA into BTA indeed resulted in increased effectiveness in different aggressive media, such as chloride and cyanide containing solutions and for different periods of time of immersion, by affecting the kinetics of the film formation. BZA results in faster formation of the polymeric film. They also supported that the use of two compounds in inhibition could be very useful in case of localised corrosion, as the film could "repair the pit before this becomes stable". The research on BTA-BZA appears very promising but it has not been tested or applied to archaeological copper and copper alloys until now.

3.10.2 Ethanolamine (C_2H_7NO)

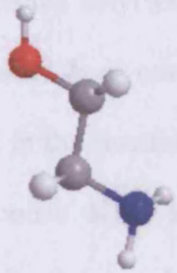


Figure 3.12. Molecular structure of ethanolamine (ETH).

Ethanolamine (ETH) or monoethanolamine (also abbreviated as MEA to differentiate it from diethanolamine) is an amine because of the amino group but also, because of the hydroxyl group in its molecule is also a primary alcohol. ETH is a weak base and is considered harmful, flammable and corrosive with an odour similar to that of ammonia (source: http://en.wikipedia.org). ETH is in a liquid form and it is irritating to skin and eyes so any contact should be avoided.

Ethanolamine has been also reported to present synergistic effect with BTA. ETH was initially used to adjust the pH levels of BTA solutions to neutral or near neutral levels.

It has been suggested that the combination of the two compounds provides the best inhibition in the pH range 6.5-7.7. The synergistic effect between BTA and ETH was attributed also to the film growth kinetics, leading to a faster film formation hindering both anodic and cathodic reactions of the corrosion process (Wang and Zhang, 1987: 2799-2806). Ethanolamine and diethylenamine have been also used for the stabilisation of iron corrosion.

3.10.3 Potassium Ethyl Xanthate ($KC_3H_5S_2O$)

Potassium ethyl xanthate (KEX) is extensively used in industry for the separation of copper minerals from other materials during metallurgical processes. More specifically KEX is used in the flotation process as a collector for sulphur-containing copper minerals such as chalcocite. KEX alters the mineral surface properties rendering the surface hydrophobic (Zdziennicka *et al*, 1998:234-239). KEX comes in the form of white or yellow pellets and it is harmful in inhalation and any contact with the skin should be avoided.

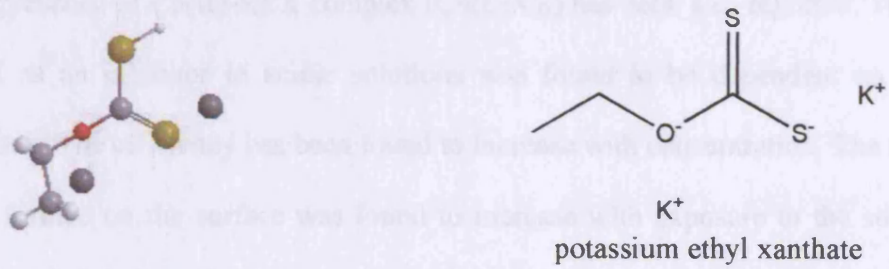


Figure 3.13. Molecular structure of potassium ethyl xanthate (KEX).

KEX has been tested industrially as an inhibitor to protect anodic dissolution of copper in acidic chloride-containing solutions. The presence of KEX in chloride containing solutions has been observed to cause a shift of the potential to more positive values. KEX was found to be chemically adsorbed onto the copper surface resulting in a hydrophobic copper surface that obstructed the reaction of copper with water (Gonzalez *et al*, 1993: 455). During the reaction of KEX with copper, the ethyl xanthate anion is oxidised to diethyl dixanthogen which forms a physical barrier on the copper surface (Souto *et al*, 1997: 510)

$$C_2H_5OCS_2^- \rightarrow (C_2H_5OCS_2)_{ads} + e^- \quad (24)$$

$$(C_2H_5OCS_2)_{ads} + C_2H_5OCS_2^- \rightarrow (C_2H_5OCS_2)_2 + e^- \quad (25)$$

The inhibition action of KEX on copper might be due to the formation of a complex with copper I on the surface. The Cu(I)-EtX complex formed blocks the metal dissolution (Scendo, 2005: 2778):

$$Cu + HEtX \leftrightarrow (Cu\text{-}HEtX)_{ads} \quad (26)$$

$$n CuCl_2^- + n HEtX \leftrightarrow (CuEtX)_n + nH^+ + 2nCl^- \quad (27)$$

$$(Cu\text{-}HEtX)_{ads} + (CuEtX)_n \leftrightarrow [(Cu\text{-}HEtX)\text{-}(CuEtX)_n]_{ads} \quad (28)$$

The presence of Cu(II)-KEX complex ($Cu(EtX)_2$) has been also reported. The efficiency of KEX as an inhibitor in acidic solutions was found to be dependent on the pH of the solution. The efficiency has been found to increase with concentration. The thickness of the film formed on the surface was found to increase with exposure to the solution (Scendo, 2005: 1738-1749). However, although KEX is portrayed as a promising inhibitor for copper in chloride containing environments (both alkaline and acidic), it was found to form a non uniform passivating layer on the surface. The presence of pits on the film resulted in localised corrosion (Gonzalez *et al*, 1993: 456). The effectiveness of KEX as an inhibitor depends on the extent of coverage of the surface it provides (Scendo, 2005: 2786). Also, in chloride containing solutions, the inhibition of copper by KEX begins from the adsorption of a KEX monolayer followed by the growth of a tri-dimensional film cuprous xanthate film (Gomez Becerra *et al*, 1987: 779-778).

The synergistic effect between KEX and BTA in chloride containing environments has been reported and confirmed in several published articles. The inhibitive action of the two compounds was tested in several concentrations and corrosive media with satisfactory

results. Souto *et al* (1996) showed that during the inhibition treatment using the mixture of BTA and KEX a Cu(I)-KEX polymeric film is formed on the copper surface, similar to that observed when only KEX was used. Analysis of the film using XPS also showed the nitrogen peak to be indicative of the presence of BTA. It was suggested that chlorides play a role in the formation of a stable passive copper-KEX film on the copper surface (Souto *et al*, 1996:161-165).

The synergistic effect between BTA and KEX was attributed to a co-adsorption of the compounds leading to the formation of a more compact and passive heterogeneous polymeric film incorporating both copper and chlorides ions. The Cu-KEX film presented some holes in the crystal lattice and it was suggested that BTA sealed these holes providing a more stable and protective polymeric film (Gonzalez *et al*, 1993: 450-456).

Hepel and Cateforis (2001: 3814) confirmed the previous results and attributed the synergistic effect to the formation of a "new two-dimensional non-stoichiometric phase: xCuBTA·(1-x)CuEtX" which is more rigid and compact.

In most cases, the copper was also anodised, which is something that was not considered in the case of testing the combination for archaeological copper surfaces.

3.10.4 Potassium Iodide (KI)

Potassium iodide (KI) has been used in combination with copper to form polymers that could be used in laser protection systems (Li *et al*, 2006: 1415). Potassium iodide has been

tested as a means to improve the inhibitive efficiency of BTA in sulphuric acid solutions because of the synergistic effect observed between them. In general halide ions can improve the adsorption of organic inhibitors on the metal substrate resulting in increased inhibitive efficiency of the compound. Therefore the presence of potassium iodide enhances the adsorption of BTA on copper (Schweinsberg *et al*, 1997: 161).

Wu (1993: 215-217) investigated the synergistic effect between BTA and KI for copper inhibition. The adsorption of iodide on the copper substrate was found to occur prior to the formation of the protective film. The addition of KI not only enhanced the adsorption of BTA onto copper due to an electrostatic force between adsorbed iodide anions and BTA cations but also resulted in the formation of a new copper-iodide-BTA (CuIBTA) complex with a molar ratio of iodide to BTA of 1: 2. The film formed was thicker than that of BTA alone. There was no information as to whether this complex is polymeric or not in its structure. One important issue is that the coverage of the surface was not uniform and more importantly the efficiency was affected by the formation of the film.

Wu *et al* (1993) suggest that since BTA is found in a protonated cationic form in solution ($BTAH_2^+$) the presence of iodide on the copper surface could improve its adsorption therefore its efficiency. Iodide could possibly form a dipole with copper orientated with the negative end in the direction of the solution. Possible explanations of the synergistic effect observed between BTA and KI could be that it is due to an electrostatic attractive force between the adsorbed on the metal iodide and BTA that improved its adsorption. Alternatively it could be the formation of a covalent bond between a noniodized BTA

molecule and the adsorbed iodide, or a positive shifting of the zero-charge potential that leads to negative charge of the metal surface resulting in improved adsorption of BTA on the metal (Wu *et al*, 1993: 2791, Schweinsberg *et al*, 1997: 161).

According the Wu *et al* (1993: 2799) the addition of KI in the BTA solution resulted in the formation of a thicker, better polymerized film that incorporated iodide, Cu(IBTA), affecting the anodic reaction:

$$pCu + mI^- + nBTAH \rightarrow Cu_p(I_mBTA_n) + 2nH^+ + pe^- \quad (29)$$

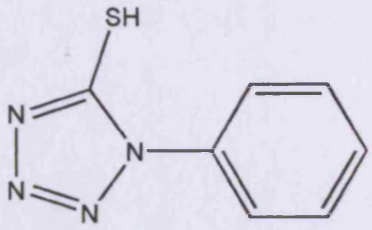
$$pCu + mI^- + nBTAH \rightarrow Cu_p(I_mBTA_n) + nH^+ + pe^- \quad (30)$$

Where p = m + n. The reaction of the protonated $BTAH_2^+$ (equation 29) is most probably favoured since the amount of BTA cation is predominant in solution by four times and iodide forms a dipole with copper. Iodide was found to react with BTA only in the presence of copper forming a cuprous-iodide-BTA polymer (Wu *et al*, 1993: 2791-2800).

KI on its own resulted in accelerated corrosion since the formation of a CuI film was proved to be unstable (Wu *et al*, 1993: 2793).

3.10.5 1-Phenyl-5 Mercapto-Tetrazole ($C_7H_6N_4S$)

1-Phenyl-5 Mercapto-Tetrazole (PMT) has been tested as corrosion inhibitor for copper-zinc alloy (70-30) and was found to be very effective in sulphuric acid media. The effectiveness increased with concentration with 10^{-3} M reaching 99% (Kertit *et al*, 1998: 2070-2082).



1-phenyl-5-mercapto-1,2,3,4-tetrazole

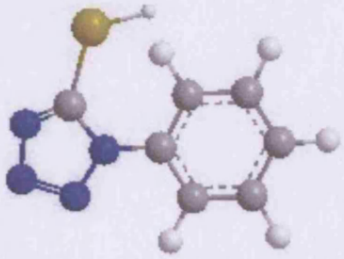


Figure 3.14. Molecular structure of PMT.

PMT was also found to be effective inhibitor for brass in nitric acid media. The results were found to be similar to those of sulphuric acid. The effectiveness was found to increase with concentration and temperature with the best results obtained at 50°C (Mihit *et al*, 2006: 2389-2395).

PMT forms a polymeric complex with copper I. Ye *et al* (1998: 307-317) found that the film was formed within the first 30 minutes of copper immersion into the solution. The effectiveness of the inhibitor was tested in different concentrations (0.003-0.0112 M). PMT has low solubility in water, so more concentrated solutions were difficult to obtain. Similarly to the previous studies, temperature was found to affect the process with the best results obtained at 20-50°C. PMT was found to be a better inhibitor than BTA in chloride or H_2S media by stabilizing Cu^+ and impeding reactions of copper corrosion. PMT is bonded to copper through both nitrogen and sulphur ions of the inhibitor molecule linking this way more than one copper ions. The film formed is hydrophobic and follows the hard/soft acid/base theory described earlier, as soft acid copper is preferably bonded to soft base such as PMT.

CHAPTER 4

4 Methodology and Experimental Design

4.1 Introduction

Modern industrial research has mainly focused on inhibitive function on uncorroded copper surfaces and the prevention of the initial stages of surface corrosion. However, most archaeological copper artefacts can represent a more advanced stage of corrosion. Furthermore, for archaeological artefacts it is often desirable to retain the existing natural corrosion or patina while preventing further corrosion of any remaining metal. Whilst published reports discuss the general mechanisms by which inhibitors work on clean metal, there is comparatively little research about inhibitor interactions and exact mechanisms in complex variable layers of corrosion products representative of archaeological copper and copper alloys.

The corrosion rate is dependent on complex, often interrelated variables between the metal and burial environment. The interface between different corrosion products is complex too, examples include intergranular corrosion of the remaining metal and variable concentrations of chlorides in pits, and nantokite (CuCl) layers underlying more stable layers of corrosion retaining the original shape, decorative patterns and surface information. Existing corrosion layers of nantokite further react to form powdery "bronze disease" which can disrupt overlying layers.

The aim of this study is to gain a better understanding of the corrosion inhibition mechanism of benzotriazole when combined with other inhibitors on corroded copper. Such research should shed light on the previously unanswered question as to why BTA treatments have been observed to fail on heavily corroded objects in archaeological or museum storage conditions. In particular, the research investigates the factors affecting BTA inhibition efficiency alone, as well as its synergism with other selected inhibitive compounds. BTA does not always function at its maximum efficiency under complex, variable conditions. Other "additives" of better performing inhibitors for chloride-containing corrosion products or low pH corrosion pits would be expected to improve overall corrosion prevention.

The experimental work is divided into two general sections. The first group of experiments involved tests of BTA solutions and examined factors such as concentration, solvent, time of immersion and number of treatments to establish control conditions. In other words, this aims to obtain more quantitative data for standard BTA treatments on pre-corroded coupons under selected test conditions as well as archaeological metals for further comparative research.

The second group of experiments examined synergism of BTA with other selected corrosion inhibitors for the treatment of corroded test copper coupons. These inhibitor combinations have not been previously used widely in archaeological conservation, but have been tested on clean copper for industrial purposes and are known to show a synergistic effect with BTA. As most archaeological artefacts are covered with complex

corrosion products, it was essential to extend existing procedures for studying the function of these compounds as corrosion inhibitors on corroded copper, rather than relying on the experiments on clean copper found in the literature (see Faltermeier, 1995 and Brostoff, 1997).

Experiments were undertaken in both laboratory accelerated corrosion tests and field conditions. The initial laboratory experiments were performed on both clean and precorroded copper coupons. The action of selected inhibitor mixtures on clean and artificially corroded copper coupons were tested for comparative reasons.

The inhibitive effectiveness of treatments was examined using accelerated corrosion tests and weight change measurements in relation to the following fundamental variables:

- Copper substrate (clean, corroded)
- Concentration of reagent solution used
- Time of immersion.

Experiments were undertaken so that direct qualitative and semi-quantitative comparisons of the results could be made. The structure of complex 2-inhibitor films was further investigated using X-Ray-Photoelectron Spectroscopy (XPS), Infra-red Spectroscopy (FTIR), and Scanning Electron Microscopy-Energy Dispersive Spectrometer (SEM-EDS).

After the initial testing on pre-corroded coupons, the more effective inhibitor mixtures were tested on archaeological artefacts excavated from the archaeological sites of Mochlos in

Greece and Kaman Kalehöyük in Turkey. The objects from these two sites were selected for different reasons that are fully explained later on in this chapter as well as in chapter 7.

4.2 Copper coupons

Testing inhibitors on archaeological objects is not appropriate because corrosion testing can be destructive, causing severe damage to an object. Accelerated corrosion tests are standardised in an attempt to ensure significant failure of at least some of the test material. Evaluation of failures is often as important as evaluation of successes. Moreover, standard industrial tests, such as salt spray, etc. should not be applied on archaeological artefacts, because of the variation found in their composition, shape and size, as well as the degree and form of corrosion affects the test results.

Experimentation on consistent material is important for more reliable and comparative results. To obtain uniform corrosion products is a complex process and the result may not always be sufficiently routine or representative for archaeological metals.

Several researchers in archaeological conservation have tried to reproduce artificially pre-corroded specimens for laboratory experiments (Angelucci *et al*, 1978; Faltermeier, 1995; Brostoff, 1997; Brazil, 1999). Angellucci *et al* (1978) produced copper coupons suffering with bronze disease in order to test the efficiency of conservation treatments. Based on the observation that the presence of nantokite generates the electrochemical reactions responsible for bronze disease, pastes made from different mixtures of CuCl and $CuCl_2$ with distilled water and a "Corrodkote test" agent consisting of $Cu(NO_3)_2$, $FeCl_3.6H_2O$,

NH_4Cl, distilled water and kaolin was tested. After being polished using sand paper and degreased in petroleum ether at 60°C the pastes were applied to the coupons and they were then left for 96 hours in a wet chamber (RH>95%). After the initial exposure, the coupons were brushed in running water and dried, before being returned to the "wet" chamber, for another 200 hours. They were then again brushed under running water, then once more placed in the wet chamber for a further 48 hours. This process produced pitting corrosion resulting in active bronze disease. The coupons were covered with some of the corrosion products found on archaeological objects but the thickness varied and there was a lack of complex intergranular corrosion pitting. Based on visual observation under the binocular microscope and macro photography, the authors concluded that the method was producing consistent coupons and could be used satisfactorily to test archaeological copper treatments (Angeluci *et al*, 1978: 147-156).

Faltermeier (1995) tested several other methods to produce corroded coupons including the Angelucci *et al* method. He concluded that the Angelucci *et al* method was not, in fact, very reproducible. He suggested another way for producing corroded copper coupons, using cupric chloride solution, which covered the coupons with a thin layer of nantokite and cuprite. This technique needed less time and the corrosion was relatively more uniform since the coupon is immersed wholly in the solution (Faltermeier, 1995: 104-105). Therefore, Faltermeier's (1995) method was adopted in this study to produce corroded coupons for the laboratory testing of the inhibitive compounds.

The size and shape of the testing coupons also has a great influence on the corrosion rate. Rectangular coupons are often preferred over circular as they are easier to cut and handle. Sharp edges can lead to the failure of a testing material. The bigger the coupon, the smaller edge to surface area ratio there is and the smaller the edge effects are (Champion, 1964: 14). The coupon size might have an effect on the overall corrosion rate, especially on pitting corrosion. In uniform corrosion, under stable conditions the effect is considered smaller (Heitz *et al*, 1992: 6).

4.3 Coupon Preparation

To keep margins of errors within the same scale for all experiments, it was essential to use coupons that had the same composition, size, and shape. Electrolytic copper (99.9% Cu) was cut into 20x50x1mm coupons, which were corroded and treated according to the technique published by Faltermeier (1995). The copper coupons were air-abraded with glass beads to remove the surface oxidation layer, degreased in acetone in ultrasonic bath, then weighed (±0.0001g) and immersed in 25 ml of 1M aqueous cupric chloride solution (dihydrate $CuCl_2.2H_2O$ in deionised water) for 24 hours at an ambient temperature of 20-25°C. The coupons were washed in deionised water for an hour (in three 20-minute baths of 100 ml for each coupon) and, after a quick immersion in ethanol, dried under an infrared lamp (approx. 50°C). Following this, the coupons were placed in an oven and exposed to 105 °C for an hour. Corrosion products could be seen to have formed on the surface. Additional X-ray Diffraction analysis of five coupons again confirmed the formation of nantokite and cuprite. XRD analysis of the coupons was undertaken using a Siemens D5000 Theta/2 Theta X Ray Diffractometer at the Chemistry Department at University

College London. The samples taken were powdered and placed evenly in between tape. The spectra were interpreted according to reference spectra and confirmed that the corrosion products produced were cuprite and nantokite.

This experimental process was chosen as an easily reproducible and reliable method available for routine production of pre-corroded surfaces for testing inhibitor combinations. The edges of the coupons, sharp from being cut, were sanded to reduce edge effects (Champion, 1964: 14). The coupons were weighed before and after each step. It was observed that the coupons gained weight during their immersion in the $CuCl_2$ solution, this weight gain varied greatly. In order to limit possible errors from this source, the coupons were classified according to the weight uptake into three groups (Table 4.1). Some coupons actually lost weight, and these were removed from testing to standardise the process as much as possible. For every experimental run, three coupons were chosen (one of each weight-gain group) as the minimum number of replicates statistically required to better define possible errors (Carter, 1982: 27). The selection of the coupons from each class was random in order to avoid bias, or standard errors. Each coupon was used exclusively for an experiment.

Table 4.1. Classification of artificially corroded copper coupons based on consistent weight gain.

Group	Weight increase % (±0.0001) (g)
1	0.0010-0.0020
2	0.0021-0.0030
3	0.0031-0.0040

The corroded test coupons were stored in plastic boxes containing silica gel. These coupons were treated with the tested inhibitors within 10 days. Specific care was taken over the

degreasing of the coupons prior to the immersion in the cupric chloride solution, as residual grease from handling during preparation can strongly affect the corrosion characteristics (Champion, 1964: 19).

Except of the pre-corroded copper coupons, clean, uncorroded coupons were also used for comparative reasons. In order to avoid the formation of copper oxides on the copper surface, the uncorroded copper coupons used for the inhibitor testing were treated within a few hours of air abrasion and degrease in acetone in an ultrasonic bath. All the coupons were handled using gloves and plastic tweezers and placed in glass petrie dishes or appropriate plastic weighing boats.

4.4 Corrosion Testing

The corrosion rate depends on variables affecting either the metal (corrosion potential, composition, etc.), the environment (such as the presence of aggressive anions), or both (temperature and humidity) (Heitz *et al*, 1992: 12). The experimental designs employed took into account the information required, the tested material (metal substrate), the type of substance to be tested and its proposed use (Carter, 1982: 3).

4.5 Accelerated corrosion testing

The objective of the experimental design was to assess inhibitor performance with a fundamental and straightforward approach that would allow the semi-quantitative evaluation of the results. However, some aspects remain subjective and qualitative. Ideally, corrosion testing would take place in an appropriate natural environment, although this is not always possible or practical due to the complexity of real conditions and the time scales

required. Furthermore, testing in real conditions is directly related to the environmental conditions, which can vary making the standardization of the results more problematic (Carter, 1982: 4). Variables like relative humidity, temperature, and concentration of air pollutants (such as SO_2 and Cl^-) may not be consistent, and would prevent satisfactory reproducibility of experimental results. Leygraf and Graedel (2000: 91) mentioned that the corrosion rate varies greatly at different exposure sites (rural, urban, industrial or marine). Factors like specimen orientation, wind direction, rain and sunshine also affect the corrosion process. Environmental conditions change over time and the corrosion of archaeological metals reflects these dynamic, changing conditions.

Accelerated corrosion tests are widely used in industry and archaeological conservation to evaluate properties of materials in relatively short periods of time. Organisations like the British Standard Institute (BSI), and the American Society for Testing and Materials (ASTM) have produced many standard procedures for testing corrosion inhibition of a variety of materials in a variety of environments. Not all of them are appropriate for archaeological metals because the conditions are too severe and do not represent museum or site storage conditions.

Accelerated corrosion testing aims to assess and compare the properties of materials in a reproducible corrosive environment. Short-term tests are used to simulate the long-term conditions experienced in natural environments by exceeding natural threshold values for RH, T, salt concentrations or air pollutants. In this case, humidity is considered to be one of the most important variables affecting copper and causing the conversion of nantokite to

atacamite and/or paratacamite. Champion (1964: 42) suggested that in order to avoid complications it is important to select a medium that reproduces the type of attack under investigation. In laboratory testing, the selection of only some of the parameters affecting corrosion permits the systematic study and the extent of the effect these have under well-defined conditions (Leygraf and Graedel, 2000: 69).

Short-term laboratory experiments should be combined with field or service trials (such as in museum display or storage conditions) to confirm results. It is difficult to correlate the information from a rapid experiment or to convert the data into real terms. One has to focus on the evaluation of a material under specific corrosive conditions.

It is common practice to test corrosion inhibitors and other protective coatings for metals using elevated RH and temperature (e.g. 95%RH, 40°C). The elevated values of RH and temperature accelerate the corrosion rate, thus shortening the duration of the experiments.

Museums and archaeological excavation storage facilities do not always have the means to control satisfactorily the environmental conditions. Furthermore, archaeological objects are not always displayed or stored according to the requirements of their material, but along with objects which consist of different materials (i.e. ceramic, wood, bone) found in the same context. Since those materials often need higher relative humidity to survive, the relative humidity is often arbitrarily adjusted to somewhere in the middle (Leygraf and Graedel, 2000: 192). Therefore, it is imperative to use corrosion inhibitors on copper metal that are effective in higher values of relative humidity.

Humidity tests are generally used to evaluate materials such as coatings and inhibitors. Cyclic humidity and temperature tests have also been used in materials testing. These tests are based on the periodical variation of RH and temperature values. This can complicate the corrosion process and more importantly could increase the experimental error given the variation in RH and temperature between different experimental runs. Static atmosphere tests are considered more reliable (Leygraf and Graedel, 2000: 71). ASTM D 2247 test is undertaken at 38°C and 95-100% RH (Meade, 2000: 542).

Following the principles of humidity testing described above, it was decided to follow the ASTM D 2247 test. The treated coupons were placed in a climate cabinet (a rather old industrial unit made by Fisons with a Eurotherm 910D dual loop thermostatic controller) and subjected to elevated relative humidity and temperature. However, the aforementioned humidity test was modified to meet the characteristics of the humidity chamber available. The humidity in the chamber was found to be unstable when the temperature was 38°C, with a fluctuation of more than ±10 % set at 95%RH. However, at 25°C the chamber was found to have less fluctuation than before (±5%). This was considered acceptable, as these conditions (75-95%RH and 25°C) are commonly used industrially (Carter, 1982: 42). Consequently, 25°C and 95% RH (±5%) was used throughout the experimental work reported here.

Some of the experiments tried to examine the relative humidity as a threshold factor which might affect the effectiveness or failure of the test materials. In those experiments, coupons

treated with inhibitors were tested at either 60±5% or 95±5% RH while the temperature remained at 25°C. A humidity/temperature sensor placed in the chamber was initially used to check that the measurements given by the chamber were correct.

The evaluation of the materials was based on simple weight-gain measurements. The assessment of the corrosion by means of weight changes is valid when applied to specimens with uniform corrosion. Weight gain measurements, widely accepted for the assessment of materials, can be used whenever the corrosion products are well adhered on the metal surface. Weight loss implies that corrosion products are removed. The removal of the corrosion products occurs with chemical etching of the surface. There is a possibility that part of the remaining metal is also removed and this can result in large experimental errors (Heitz *et al*, 1992: 12). Weight loss experiments where corrosion products are removed before weight measurements were not applicable for experiments in these studies as removing any of the corrosion products would preclude the continuous monitoring of significant coupon weight changes. Additionally, the time needed so that the weight loss of metallic copper is meaningful was out of the scope of the present experimentation.[1]

The formation of corrosion products results in a sample net increase in the mass. The weight gain is related to the thickness of the corrosion (Heitz *et al*, 1992: 12). Consequently, the mass change over time during the accelerated corrosion tests is an indicator of the corrosion rate. This can be measured using the following relationship (Skerry, 1985: 5):

[1] Wu *et al*, 1993: 2793: "Furthermore, the weight loss measurements includes the weight gain resulting from the incorporation of the inhibitor molecules and other solution species into the film"

$$IE\% = [(CR-CR_i)/ CR] \times 100 \quad (31)$$

Where

IE is the inhibitive efficiency,

CR is the weight changes of the untreated coupons, and

CR_i is the weight change of the treated coupons.

The short-term accelerated coupons can give an indication about the corrosive behaviour of a material in the future, but this data cannot be converted satisfactorily into a real-time prediction of corrosion rate.

4.5.1 Monitoring

The treated coupons were placed in the humidity chamber and were monitored by weighing (±0.0001g) at regular intervals: at 24, 48, 168, and 441 hours of exposure, and some at 840 hours.

4.6 Experimental method

Many variables influence the inhibition process, which had to be taken into account in advance before setting up an experiment. The most common method used for testing materials is to examine each variable on its own. This way only one factor at one time changes in every experiment, whilst the others are preset. However, the amount of time needed to carry out all the experiments required to examine every factor affecting the process prevented the use of such approach. Also using this approach the interactions between the factors are not examined resulting in incomplete or biased information (Grove and Davis, 1992:3). Chemical systems, such as inhibitors, are influenced by many

interrelated factors. Therefore, it is imperative to evaluate not only each factor alone, but also the interaction between factors to fully understand the corrosion inhibition mechanisms.

Statistically designed experiments allow the alteration of many factors at each experiment. The effects of the main factors and their interactions can be assessed in a systematic way leading to comprehensive and reliable results. Moreover, using statistically designed experiments minimises the number of experiments needed to evaluate a process.

The aims and objectives of each experiment have to be planned thoroughly beforehand to avoid unnecessary complexity. Following this, one has to select the factors to be tested. A factor is defined as any variable in an experiment that might affect the result (Morgan, 1991: 50). The factors should be tested at a range of values. These values are called levels of a factor, and are represented either with numbers (1, 2, 3, etc.) or with + and - symbols. The factors depending on their nature can be qualitative or quantitative. Qualitative factors are those that cannot be measured on a scale, such as something absent or present or the type of substrate (e.g. clean or corroded copper) whilst quantitative are the ones that are measured on a numerical scale (such as temperature or concentration). It is better not to test all factors at all possible levels in one experiment. The result of an experiment could exclude some factors from subsequent experiments. For the factors not affecting the process one can carry on keeping the value that is the most affordable (Grove and Davis, 1992: 3-4). Therefore, it is helpful to carry out some preliminary tests to eliminate certain

factors in order to continue experimentation only with the significant ones (Morgan, 1991: 89).

The assessment of an experiment is based on the outcome of the experimental runs, called response, measured on a numerical scale (Morgan, 1991). In this case the weight change % was the response chosen to evaluate the effectiveness of the inhibitors. The weight uptake % is inversely proportional to the effectiveness of an inhibitor. Therefore, the greater the weight uptake of a treated coupon after exposure to high relative humidity, the less effective the treatment. [2]

Having established the experimental question, the factors, and the response, one has to decide about the experimental design to be used. There are many models available in the literature. The design of an experiment depends on the number of the factors to be tested as well as the number of levels. The most common is the testing of two levels for each factor. The total number of runs (N) in a two-level factorial design is $N = 2^f$ where f is the number of factors tested (Morgan, 1991: 92). The more levels there are in an experiment, the more complicated the analysis of the results.

Each factor at each level is examined exactly the same number of times, leading to balanced experiments. If not all of the experiments are run the design will be unbalanced and the results not valid (Morgan, 1991: 89). After the completion of the experiments, the results can be assessed using statistical methods when appropriate assumptions are checked

[2] Originally, the IE% was chosen as the response of the experimental runs. Because there were coupons, which did not take any weight, it was mathematically impossible to proceed using it and therefore the weight change was used. The IE% showing the effectiveness of the tested treatments are also presented.

(e.g. normal distribution). Common sense has to be used along with the statistical analysis for the interpretation of the results (Grove and Davis, 1992: 8).

The above-mentioned stages as recommended by Montgomery (1997) are shown in table 4.2

Table 4.2 ***Guidelines for statistically designed experiments (after Montgomery, 1997: 14)***

1.	Recognition of and statement of the problem
2.	Choice of factors and levels
3.	Selection of the response variable
4.	Choice of experimental design
5.	Performing the experiment
6.	Statistical analysis of the data
7.	Conclusions and recommendations

Even when experiments are carried out under the same conditions there are variations in the results (Box *et al*, 1978: 24). When conducting an experiment, it is very important to minimise the errors resulting from the procedure that could lead to incorrect or biased results. Only a small part of the errors are measurement errors. Most of the errors are related to experimental errors. Experimental design and statistical analysis of the data help diminishing these errors (Box *et al*, 1978: 7). Apart from the factors chosen to be tested and which can be controlled, there were others which are uncontrollable (e.g. environmental temperature). To avoid systematic errors due to uncontrolled factors during the procedure, the experimental runs (treatments) should be carried out in random order (Morgan, 1991: 51). In this case, all the treatments happen almost simultaneously to avoid alterations in environmental conditions which could affect the outcome.

All the tested treatments were applied to a minimum of three coupons. The replicates and any variation in the results permit the estimation of possible experimental errors.

Unfortunately, it was not possible to test all the possible variables affecting the inhibition efficiency within the given timeframe of this PhD research. There were uncontrolled factors such as the environmental temperature at which the experiments were performed. The effect of uncontrollable factors is reflected in the variation of the results of the replicates. Although the fluctuation of the temperature in the laboratory was not great, it was still an uncontrollable factor. To eliminate the effect of the temperature all the treatments of an experiment took place under the same conditions, at the same time. The effect of the uncontrollable factors can be also seen in similar treatments carried out at different times of the year where there is variation in effectiveness.

4.6.1 Experimental design

Various experiments were performed to evaluate the most important selected factors affecting inhibition efficiency. In general, using statistically designed experiments, it was easier to distinguish the factors that affected the corrosion inhibition of copper (real factors) from those that affected the process accidentally, due to experimental error. The factors tested were the BTA concentration, the repeated use of the BTA solution, the presence of additives within BTA solutions and their concentration, the solvent, the time of immersion, and the substrate.

In Chapter 5, the experiments about BTA and factors affecting its efficiency (substrate, BTA concentration, solvent, and time of immersion) are presented. Chapter 6 examines the synergism between BTA and additives. The initial experiments were performed using the concentrations recommended in the literature followed by experiments using higher concentrations. The choice of concentration was based on the BTA concentration and respective solubility of the inhibitors in the solvents. The factors and their levels are described for each experiment at the respective chapters.

4.6.2 Statistical analysis

There are many ways to analyse the results of an experiment, the most common of which is the analysis of variance (ANOVA). ANOVA methods are used to analyse multi-factorial experimental designs, to examine the way factors or combination of factors interact, if the factors are significant or not, and their effect on the overall process. Using ANOVA the different sources of variation are quantified and calculated distinguishing the variation due to factor effect from the accidental variation due to experimental error. ANOVA can assess the variance of the data either by using the between the treatments means or by using the within the treatments means by making use of an F-test. F-test is a numerical method used to assess whether the variance of the responses resulting from the difference of the numerical means is greater than the random variation of the data. In other words, F-test is a method to determine which effect is real (Morgan 1991: 20). ANOVA also allows estimation of errors. ANOVA tables consist of the total sum of squares of the results, the F value (which indicates if the hypothesis is correct or should be rejected), the probability and

the residual error sum of squares for each variable in relation to the degrees of freedom (which are related to the number of replicates used).

A factor (e.g. concentration of the BTA solution) has a significant effect on an experimental process when the change of levels results in change of the outcome. The effects of the main factors and the interactions between the factors are represented by graphs based on mathematical formulae (Montgomery, 1997: 228). The statistical analysis of the data can be illustrated graphically with main effect plots, interaction plots and normal probability plots. This graphical analysis is based on mathematical formulae and makes the distinction of the significant and insignificant variables clearer.

The main effect plots result from the difference of the responses at the two levels (in case of a two-level design) divided by two. In 2-level factorial designs the plot consists of a line connecting the average response of the levels. This line represents the effect of the factor. The larger the effect the bigger the distance between the levels is, therefore the line itself has a high gradient. If a factor is not significant the line in the graph will be small and near horizontal. The effect of the factor is also measured by comparing the responses. The difference of the responses shows which level gives better results (Grove and Davis, 1992:7, 26-27).

Similarly, the interaction plot for two factors A and B, result from the difference of A for B^+ and A for B^-, divided by 2. When the effect of one factor depends on the level of another factor there is interaction between them. Interaction between factors happens when

the effect of altering the factors at the same time is different from the sum of the effects when each factor is altered separately. In an interaction plot the interaction of two factors is represented by two lines, which cross or will cross when extended. If there is no interaction between the two factors, the lines are parallel to each other (Grove and Davis, 1992: 25-28).

Normal plots or normal probability plots are used to identify the most important variables affecting the experimental response. In these graphs the main and interaction effects are plotted. The factors not affecting the outcome fall in a straight line whilst the factors/interaction of factors affecting the outcome fall outside the line. This way the significant effects can be distinguished from the insignificant. Depending on which part of the line the points are, the effect can be negative or positive. Also the further out of the line a point is, the bigger the effect.

4.7 Testing on archaeological artefacts

The aim of the testing on archaeological artefacts was to verify the results from the simulation corrosion testing with more complex corroded copper alloy objects. Testing took place in the conservation laboratories of the excavation sites. Selected objects, with agreement of the excavation directors Prof. Soles (Mochlos) and Dr. Omura (Kaman Kalehöyük) treated objects were subjected to high relative humidity (almost 100% RH) for 24 hours to test the efficiency of the treatments. The objects were placed in closed plastic containers, containing deionised water soaked cotton which resulted in 100% relative humidity. RH cards allowed the monitoring of the humidity. Based upon the laboratory results on mixed inhibitor performance, the more successful treatments of inhibitors were applied to objects excavated at two different archaeological sites in Greece (Mochlos) and

Turkey (Kaman Kalehöyük). The sites are dated to different periods and bring to light different types of copper alloy artefacts. Mochlos is a Late Minoan coastal site while Kaman Kalehöyük is inland and covers a longer chronological period (Early Bronze Age to Islamic period). Although the objects have been excavated from sites with completely different environments, all suffer from bronze disease and are heavily corroded.

Analysis of the film formed on the archaeological objects was not possible, and weight changes were of no use given the complexity of the corrosion and often friable nature of corrosion products present. Consequently, the evaluation of the treatments was based foremost on visual observations with statistical analysis of subjective ranking criteria. The basic criterion for this evaluation was the extent of bronze disease outbreaks occurring on the objects after the 24-hour exposure to high RH%.

A method commonly used in corrosion testing is a simple nominal method, or fail/pass test, where a specific characteristic or corrosion form is chosen (Carter, 1982: 11). For example, the objects which show renewed active corrosion after the testing fail, while the ones with no signs of corrosion are rated as pass. This method detects the presence of corrosion but not the extent of corrosion of an object after the testing, thus, it was imperative to select a scale that could allow a more objective, closer to reality evaluation of the treatments. Such scales are used in museums to classify forms of corrosion and to define conservation priorities. Consistency is a key point when using Criterion Anchored Rating Scales (CARS) (Suenson-Taylor *et al*, 1999: 184-194). One has to know the object of the study well enough to be able to recognize the differences. The objective of creating a scale is to assist

the consistency of the results and the judgement (Saaty: 1990: 7) Saaty: 7"to obtain better estimates of reality we should channel our impressions, feelings, beliefs in a systematic way in providing judgements. The object is to enhance objectivity and downplay too much subjectivity".

A more detailed scale describing the degree of corrosion was created in order to assess the treatments. Active corrosion depends on the form and extent of corrosion of the object, which is related to the composition of the metal alloy, the method of production (e.g. cast or hammered, cold worked or annealed, etc.), the burial conditions, and many more factors that cannot be analysed due to the complexity of the archaeological objects.

Fundamentally, the scale cannot take into account all the factors affecting the result as aforementioned. However, the number of the objects used (e.g. 10 for each treatment at Kaman Kalehöyük tests) can give a close approximation of reality.

The scale was divided into 5 depending on the extent of bronze disease outbreaks found on the objects. At the end of the treatments, the evaluation was according to

i) The total number of artefacts with pitting corrosion

ii) The severity of the corrosion found (the number of pits).

Each level was given a different score. Level 0 refers to objects with no corrosion. The number of objects of each group at each level was multiplied by the score and finally the numbers from each level were summed. The final number is nothing but a subjective degree of corrosion. This number does not represent the actual degree of corrosion.

Moreover, in pitting corrosion, measurements such as the depth of the pit, etc. have to be assessed in order to calculate the overall corrosion.

Table 4.3. Scale used for the assessment of the treatments on archaeological objects from Mochlos and Kaman.

Level	Degree of corrosion	Score
0	No corrosion	0
I	Minimum bronze disease (BD) outbreaks (up to 4 small spots)	1
II	Few BD spots (>4)	2
III	BD in a larger extent	3
IV	BD overall	4

4.8 Restrictions and Limitations

Copper and copper alloy archaeological artefacts are covered with a variety of corrosion products, the nature of which is dependent on many factors such as the composition of the metal or alloy, and the burial environment. As already mentioned, the presence of corrosion products on the metal surface affects in general the inhibition mechanism. The heterogeneous multi-layers of corrosion found in archaeological objects cannot be duplicated exactly in the laboratory, in a reproducible manner. Corrosion layers formed on archaeological objects are often damaged during lifting.

The tests undertaken on coupons covered with single corrosion products (nantokite and cuprite) were therefore, a simplified model. A model was chosen that reproduced the variables which affect corrosion and inhibition to the greatest extent.

The copper coupons used were composed of 99.9% copper. As a result, the effect of these inhibitors on copper alloys was not studied in these experiments. It has been suggested that BTA does not form complexes as readily with some other metals. Ammeloot *et al* (1998: 233) suggest that BTA is bonded to copper and does not affect tin when applied on copper-tin alloys. Similarly, Combarieu *et al* (1998: 228) found that BTA forms complexes only with copper and not zinc when applied on brass. To date, there is limited research on the compounds and complexes BTA forms with other metals and especially with complex, mixed corrosion products.

4.9 Analysis of copper-inhibitor complexes

Several analytical techniques were used to investigate the mode of action of the different inhibitors and inhibitor mixtures as well as how they complex with copper. The techniques adopted offered different information or perspectives, about the chemical and physical properties of the inhibitor films formed on the copper specimens. The basic principles of selected analytical techniques and the methodology followed are presented to assess the quality of the compositional data.

4.9.1 SEM-EDS

The scanning electron microscope (SEM) is a great imaging and characterization tool allowing the examination and analysis of a material. The surface of a sample is scanned by a fine beam of electrons resulting in the emission of secondary and backscattered electrons. Secondary electrons (SE) are incident electrons irradiated from the sample in energies up to 50 eV, are collected by a detector and can give information about the topography and chemistry of the surface analysed. Backscattered electrons (BSE) are the primary electrons

scattered within the sample and vary with the atomic number providing information about the chemical composition of the specimen (Amelinckx *et al*, 1997: 310, 314-315).

Analysis of a sample can also take place by using an energy dispersive x-ray spectrometer (EDS) which enables quantitative elemental composition analysis by measuring the x-rays emitted by the specimen. EDS measures the energy and the intensity distribution of the elements.

The SEM-EDS analysis took place at Wolfson Scientific laboratories of the Institute of Archaeology, UCL using a JEOL JSM-35CF with Link ISIS microanalysis system. SEM-EDS provided information about the topography of the copper inhibitor films and the way they were structured on both clean and corroded copper surfaces. The samples that were analysed with JEOL SEM were not carbon-coated since one of the basic elements of the inhibitors was carbon and it was necessary to see its distribution on the surface using linescans. Linescans were performed to examine the distribution of the elements (Cu, O, C, N, S, K and I) on a line. This analysis provided both qualitative and quantitative data along a line. These data although provide more information about the way the elements are distributed on the surface, cannot be considered absolute since this method is not accurate (accuracy of analysis on polished samples is about 1%) when used for analysis of light elements (i.e. C, S, O, N). Another drawback regarding the accuracy of the quantitative results is the depth of analysis. The inhibitor films are very thin (usually measured in nm) and the area analysed by SEM-EDS is around 1-2 μm. The compositional analysis of the samples results in high percentages of copper (98-99%). The analysis of the copper-

inhibitor samples should be used only to identify comparative distribution trends in relation to the surface topography.

Imaging of the treated copper specimens also took place by using Hitachi s-570 SEM. These samples that were used only for optical observation of the surface were gold-coated to obtain a better quality image.

4.9.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared Spectroscopy is a technique based on the vibrations of the atoms of a molecule interacting with infrared light (Stuart, 1996: 1). The outcome of the analysis is a spectrum obtained when infrared radiation passes through the substance analysed. The different chemical groups in a molecule absorb infrared radiation and the peaks of the spectrum represent chemical bonds expressed in wavenumber (cm^{-1}) on the X-axis. The Y-axis can be plotted either in absorbance or in transmittance mode. Absorbance mode corresponds to the amount of infrared radiation absorbed by the molecule and it is used for qualitative analysis. Transmittance mode corresponds to the infrared radiation the molecule transmits and it is used only for qualitative analysis. The relationship between absorbed and transmitted radiation of a molecule is:

$$A = \log (1/T) \qquad (32)$$

Where

A is absorbance and T transmittance (Smith, B, 1998: 5-6).

A functional chemical group in different molecules absorbs infrared light at the same wavenumber.

Fourier Transform Infrared Spectroscopy (FTIR) is a more advanced technique of infrared spectroscopy where the beam coming from the source is divided by a beam splitter before passing through the sample. The beam from the source is partly transmitted and partly reflected by two mirrors placed one across the source and one perpendicular. The mirrors reflect 50% of the beam back to the source and 50% is transmitted back to the beam splitter. The latter beam passes through the sample at 90° and is measured at the detector (Stuart, 1996: 25).

FTIR was selected because it provides a wide variety of analytical possibilities. Many different preparation methods and techniques can be used to answer different experimental questions. Some of the most important advantages of the technique is that can be used to analyse almost every substance in several possible forms (solid, liquid, gases) and the spectra can provide information about the chemistry of a molecule. Another advantage of the technique is that only a small sample of a compound is needed for the analysis. It is also a fast and comparatively cheap analytical method.

One of the disadvantages of the technique is that it can only analyse compounds with molecules, which have chemical bonds. The greatest disadvantage of the technique, which is of interest in this case, is that it is not the best method to analyse complex compounds. If a mixture is analysed, it is difficult to distinguish and understand which peak, therefore,

chemical bond, belongs to which compound. It is also hard to analyse aqueous solutions because water strongly absorbs infrared radiation. Moreover, water dissolves most of the transparent materials (i.e. KBr) used in the analysis (Smith, 1998:2).

4.9.2.1 Aims of the analysis

The aim of the analysis was to understand how the different inhibitors complex with corroded and clean copper as well as in case of inhibitor combinations the way they react with copper and whether there is any type of interaction between them. As it has been mentioned, analysis of mixtures of compounds is not straightforward consequently the results can be examined only comparatively using the spectra of the pure compounds as reference for the interpretation.

Different methods and techniques were used in order to facilitate the interpretation of the analytical results. When a complex mixture is analysed it is hard to determine which bands are related to which molecule or to which inhibitor. To overcome this problem, each compound was first analysed alone and compared to standard spectra, then in combination with another compound.

The analysis took place at the Wolfson Laboratories of the Institute of Archaeology using a PERKIN ELMER System 2000 FT-IR. Each of the techniques adopted gave information of the chemical bonds of the compounds and the way they react when applied to copper.

4.9.2.2 Methods

4.9.2.2.1 Transmittance (KBr pellets)

Potassium bromide (KBr) mixed with the sample was used in the transmittance mode. One of the advantages of the technique is that only a small quantity of the sample is needed (Colthup *et al*, 1990: 89). The solid inhibitive compounds were ground using a mortar and pestle and then mixed with potassium bromide (KBr) and pressed into pellets/disks using a hand-operated press. The pressure used was approximately 10 tons for a minute. The inhibitor concentration used, was between 1-3 % depending on the compound. KBr is transparent and since the inhibitors are colourless the disks were clear. The disks were 1cm in diameter and approximately 1mm in thickness. BTA, AMT, KEX, PMT and KI that are in powder form were prepared using this method.

ETH and BZA are in solution so a drop of the compound was placed on a KBr disk and dried under infrared lamp (approx. 50°C) for 30 minutes. Higher temperature could cause alterations to the compounds. KBr is highly hydroscopic and additional care was taken to mix it with the compound and create the disk under dry conditions. The disks were opaque in appearance when moisture was present that would affect the analysis.

4.9.2.2.2 Analysis of inhibitor solutions

The solutions were analysed using a Zinc Selenide window. This is in a form of yellow crystals of granular powder and has M.P. at 1515°C. It is quite toxic (TLV 0.2 mg/m3 as for selenium compounds) (MSDS safety data, 2006). Since zinc selenide is water-soluble, only non-aqueous solutions could be analysed. Both the pure solutions (inhibitor-ethanol) and the solutions after the immersion of copper were analysed. The aim was to check if any

copper-inhibitor complex forms within the solution. The solutions analysed are given in chapters 5 and 6. After each analysis the window was thoroughly rinsed with ethanol (Analar grade).

4.9.2.2.3 Reflectance

It was found necessary to analyse the copper-inhibitor film not only in powder form mixed with KBr but directly on the copper coupons. Of great importance was to understand the difference of the films found on clean and corroded copper. The factors examined were the same as in the accelerated corrosion testing (substrate, inhibitor concentration used, solvent, and time of immersion). The coupons were prepared using the same methodology used for the accelerated corrosion tests. The copper coupons were immersed in the inhibitor solution for an hour or 24 hours and dried under infrared lamp. They were allowed to cool and a small piece was cut and placed on the chamber. The technique used was diffusion reflectance. The interferometer was first aligned using a mirror.[3]

4.9.3 X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) is a technique widely used for surface analysis and can give qualitative and quantitative information about the existing elements. It can provide information about the

[3] "Alignment is the adjustment of the interferometer mirror angles to optimize the amplitude of the interferogram centerburst. This is achieved by maximizing the energy of the region of the interferogram around the centerburst. The Align command aligns one mirror in the interferometer in order to achieve this". Perkin-Elmer Spectrum v3.01.

chemistry, organisation and morphology of all the elements found on the surface with the exception of H and He (Ratner and Castner, 1997: 45).

When a surface is irradiated with photons, the energy of the photons is transferred to its core-level electron, followed by the emission of the electron. The electrons are emitted according to the energy, which depends on the atom and molecule present. Each element has a threshold energy level that has to be exceeded in order to have photoemission. Above the threshold energy the emission of the electrons will be proportional to the rate of the excited photons (Ratner and Castner, 1997: 43-47).

XPS is based on the energy hv of a photon transferred to an electron of an atom resulting in emission of the electron. The kinetic energy (KE) the electron is ejected is measured by the X-Ray spectrometer:

$$E_k = hv - E_B \qquad (33)$$

Where Ek is the kinetic energy of the ejected electron, hv is the energy of the X-ray source, and E_B the binding energy of the electron in the atom of the surface analysed. The kinetic energy can be easily converted to binding energy ($E_B = hv - E_k$). Binding energy is measured in electron volts (eV) and depends on the type of atom as well as the atoms it is bound to. The binding energy is related to the covalent or ionic bonds of the atoms, which are represented on the spectra with binding energy or chemical shifts (Ratner and Castner, 1997: 47).

A target impinged by a high-energy electron beam produces the X-rays used. This includes fluorescence X-rays that are used for XPS analysis and electrons. In practice, the photon energy ranges used are Al Ka at 1486.6eV and Mg Ka (1253.6eV) X-ray emissions. In order to get meaningful information by analysing the energy of the photoemitted electrons, the photon source should be monochromatic to eliminate electrons Bremsstrahlun and satellite X-ray from reaching the sample (Woodruff and Delchar, 1994: 129-130). One of the disadvantages of the monochromatic source is that the intensity of the x-rays irradiating the samples is much lower. In order to surpass this, one can increase the power significally or use a large crystal. (Rivière, 1994:58). The sample can be also placed closer to the X-ray target (Ratner, and Castner, 1997: 76-77). A thin (approximately 10-30 μm) Al or Be window is placed on the sample to eliminate possible detection of secondary electrons from the X-ray source and contamination of the sample (Woodruff and Delchar, 1994: 130).

The energy levels XPS analysis is based can be simply classified as core levels, valence levels and Auger series (Briggs and Rivière, 1994:113). The core levels peaks are the ones related to the electron state of an atom and do not depend on the fact that the atom is not free but part of a solid surface (Briggs and Rivière, 1994: 126-7). Because the core levels are representative in energy of the atoms present, the peaks on a spectrum can provide information not only about the composition of the surface but also the position of the peaks gives information about the chemical state of the elements (Briggs and Rivière, 1994: 139).

The valence levels are related to electrons with low binding energy. These are found in the spectrum as a band consisting of smaller peaks and are dependant to the density of states.

These bands can give structural information about details unattainable by core-level bands (Briggs and Rivière, 1994:115, 123-124).

The irradiation of a surface using X-rays can result in emission of Auger electrons. Auger electrons are different from the photoelectrons. One of the differences is that the energy of Auger electrons is not dependent on the energy of the source used while photoelectrons are directly proportional to this energy as it can be seen from the equation (33) (Ratner and Castner, 1997: 48). The importance of the Auger series is that they can determine the chemical state of an element. From the four types of Auger series found in XPS, mainly the KLL series were used for this analysis. KLL series are complex and their intensity change according to the atomic number (Briggs and Rivière, 1994:117).

Other peaks found on a XPS spectrum are satellite and ghost peaks. Briggs and Rivière (1994: 127) mentioned that the satellite peaks are related to the fact that typical X-ray sources are not monochromatic and even magnesium and aluminium targets produce lower intensity lines, known as X-ray satellites. The X-ray ghost lines in an XPS spectrum are produced by impurity elements in the X-ray source.

Having discussed the basic principles of XPS analysis, it is essential to refer to the main characteristics of a spectrum. Analysis starts with a wide scan spectrum (survey scan), which covers a large area (more than 1000eV). Following this, analysis can focus on individual peaks and their features, which cannot be observed from the wide scan. The binding energy is on the x-axis and the counts on the y-axis (Ratner and Castner, 1997: 67).

Also with XPS one can carry out quantitative analysis of the elements found on the surface. The peak area of each element is measured resulting to the percentage (atomic) of each element. Usually either the percentage or the ratios between elements are measured. This quantification cannot be taken as absolute, but only as a relative scale. This method assumes that the surface is homogeneous and does not take into account factors such as the contamination layer found on almost every surface, the fact that the different libraries (some of which are theoretical and some empirical) can give different results, and other inconsistencies related to the instrument and/or the operator. Therefore, the results of this analysis should be considered semi-quantitative and therefore used with caution. The Scofield library was used for the quantification. The quantification of the elements was done using Shirley for the background subtraction.

XPS analysis of the samples allows not only examining the oxidation state of copper in each treatment, but also gives information about the element bonded to copper, to BTA and other inhibitor films.

Copper coupons treated using the method adopted for the accelerated corrosion testing were analysed. The samples were put in the chamber with an aluminium mask. Additionally, the inhibitors were analysed on gold-coated glass for comparative reasons.

A VG ESCALAB 220i XL instrument using monochromatic Al Kα radiation (1486.6eV) of 600 or 1000 μm spot size was used at the Chemistry Department of UCL.

The analysis of the coupons treated with different inhibitor solutions allowed to investigate how several factors, also examined using accelerated corrosion testing, affect the copper-inhibitor complex formed on the surface, therefore the inhibitive efficiency. The software used for the editing of the XPS spectra and the quantification of the elements was Thermo Avantage demo, kindly provided by Tim Carney of VG.

4.9.4 pH measurements

The pH of aqueous solutions of the inhibitors used was measured to examine any relation between the effectiveness of an inhibitor and the pH. It has been reported that the pH of the BTA solution drops as low as 2 when applied on heavily corroded copper and this might affect both the polymerisation and formation and of the Cu-BTA film. Some of the additives tested work synergistically with BTA by adjusting the pH of the solution.

A Corning pH meter 240 at the Chemistry Department of UCL was used. The results are presented in the following chapters.

4.9.5 Colorimetric study

In spite of all the efforts undertaken to use materials that do not cause any changes in composition or appearance of a metal object, certain treatments and/or materials can result in colour alteration of some corrosion products. For example, BTA causes slight darkening of certain corrosion products. The terms used to describe colour are the hue, which is the actual colour or the object, the value, describing the lightness or the tone of the colour and the chroma which is the intensity of the colour. The perception of colour is a subjective

matter depending on a number of factors such as the light illuminating the object, the actual surface of the object and its absorption/reflection properties and the observer (Timar-Balazsy and Eastop: 1998:82).

There are many studies and many different systems used to objectify the colour measurement. The system used for the purpose of this thesis was that defined by Commission Internationale de l'Eclairage (CIE) the main principle of which is that equal amounts of blue, green and red give white (blue-X + green-Y + red-Z = white) and any colour is expressed as the sum of these colour in proportion. The CIE system can express a colour in a two-dimensional space. A disadvantage of this method is that is does not include the lightness of the colour. Another method that includes all parameters (hue, lightness and chroma) is the CIELAB system which makes use of three coordinates, L*, a* and b* that are calculated from X, Y and Z described earlier. L* measures the lightness and a* and b* the colour. These coordinates take positive or negative values. Positive value of L* means lighter and negative darker, in case of a* positive means red and negative green and for b* positive is yellow and negative is blue. The difference in colour between two different samples is calculated using the ΔE formula: $\Delta E = (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ (Ohno, 2000).

The colour alterations caused to the coupons during the treatments were therefore assessed using a Minolta CR-221 chromameter. The chromameter has a light source C, a 45° illumination angle and measured area of 3mm. Each coupon was measured in three different spots. After each measurement the chromameter was calibrated with a white standard provided by Minolta. ΔE was calculated using the average ΔL*, Δa* and Δb*

values of the reference, untreated coupons. The greater the ΔE value is, the greater the colour changes. However, it is worth mentioning that in some cases ΔE is not always enough to describe a colour change.

All the laboratory experiments examining and assessing the way certain variable affect the inhibitive efficiency of the inhibition process in combination with pH measurements and the various analytical techniques used, aim to gain a better understanding and wider perception of the complexity of different inhibitors when used on clean and corroded copper.

CHAPTER 5

5 Benzotriazole

5.1 Introduction

Benzotriazole is a very popular inhibitor for copper not only in the field of conservation of historic copper artefacts but also in industry. The use of BTA as an inhibitor for copper for industrial applications has been fairly thoroughly investigated although there are still some unanswered questions regarding its exact mode of action on metallic copper or copper surfaces covered with corrosion products. In conservation although the use of BTA is common practice, the exact application methodology varies according the organisation and/or the conservator carrying out the treatment. The way that BTA works on archaeological copper objects covered with a number of corrosion products is not yet understood as research in this area is limited. The purpose of this chapter is to deconstruct the inhibition process of BTA by examining lesser known factors that might affect its efficiency.

One of the objectives of this chapter was to examine and assess fundamental issues regarding corrosion inhibition treatments using BTA. Factors such as concentration of the solution used, time of immersion and solvent were examined using accelerated corrosion tests using clean and artificially corroded copper coupons covered with copper chloride (nantokite) and copper oxide (cuprite). The evaluation of the accelerated corrosion testing was based on weight changes.

The accelerated corrosion testing formed the base for the analytical work carried out using SEM-EDS, FTIR and XPS. These analyses were carried out to analyse the Cu-BTA complex formed on the surface and investigate potential variations in composition depending on the variables applied each time. The aim of the analysis was not only to understand how BTA reacts with copper and how different variables can affect the formation of the copper-BTA films formed on copper surfaces but also to assess the direct relationship between the type of Cu-BTA complex formed and its inhibitive efficiency on both clean and corroded copper.

This work also provided the foundation for the next phase of this research which was the examination of other compounds that could act synergistically with BTA to improve the overall inhibitive effectiveness for the treatment of actively corroding copper.

The chapter is divided into two main sections, the first details the actual experiments and the second part describes the analysis carried out on copper coupons treated with different BTA solutions. The results of each section are discussed at the end with a view to discerning patterns of Cu-BTA formation according to the treatment method used on the copper.

5.2 Accelerated Corrosion Tests

In the first part of this chapter accelerated corrosion testing performed on both clean and artificially corroded coupons treated with different BTA solutions is discussed. Different practical aspects of application that might affect BTA performance were examined in a

series of experiments in order to understand the way in which they influence the overall outcome. The results of the experiments allowed the assessment of the effect of each factor independently as well as their interrelation and interaction with other factors. Factors such as the concentration of BTA, the solvent and the time of immersion have an effect on the Cu-BTA film formation and subsequently the inhibitive efficiency.

To evaluate the variables affecting the effectiveness of BTA statistical full factorial experiments were performed on copper coupons. The use of statistical methods in the organisation of the experiments allowed the evaluation of each variable on its own, the interaction between certain variables and finally, eliminated possible errors in the evaluation of the treatments. All the experiments were designed using Minitab 12.1 software.

Colour changes caused by the different treatments on both clean and artificially corroded coupons are also discussed in this section.

Although the experiments were performed on both clean and corroded copper coupons, the experimental work presented in this chapter focuses foremost on the artificially corroded coupons. No substantial results on the efficiency of the treatments on clean copper were obtained within the timeframe of this work. Time restrictions did not allow an extended exposure of the clean coupons on high relative humidity and no other type of accelerated tests were performed for reasons of consistency and lack of availability. [1]

[1] More rigorous testing was necessary for the clean copper coupons. Cyclic tests or salt spray tests could assess better the treatments, however these were not available. Another important issue is that the aim of the

The coupons were immersed in the inhibitor solutions for their delegated time period, following this they were dried under an infrared lamp (50°C for approximately 5 minutes). They were then stored with silica gel in a sealed polyethylene box for approximately 10 minutes to cool down, then weighed before and after the treatment with different BTA solutions. The concentration of BTA was measured in moles for consistency. To avoid systematic errors during the experiment, the coupons of each experiment were all treated simultaneously. This way unforeseen uncontrollable environmental or other factors would have the same effect on all the tested treatments and the results would be genuinely comparable. Controls in the form of untreated copper coupons were also placed in the chamber alongside the treated coupons of each experiment to be used for the calculation of the inhibitive efficiency. The coupons were numbered and their placing within the chamber randomly arranged to reduce any bias from the chamber space itself. Weight change measurements took place at regular intervals and were used for the evaluation of the treatments.

Each experiment is presented with the design used, the results, statistical analysis and a discussion of the results together with the colour changes observed. The complete set of tables with the treatment, the weight change %, inhibitive efficiency %, ANOVA and main factor and interaction plots of the experiments are given in Appendix 1.

experiments was to evaluate the treatments comparatively to each other. Different testing methods could not allow this.

5.3 Artificially Corroded copper

5.3.1 Experiment BTA 1

The application methodology for BTA treatments used on archaeological objects varies depending on the practice of the museum or the conservation laboratory. [2]

In the first experiment the factors tested were the time of immersion and the concentration of BTA. The factors and the values chosen (levels) are shown in table 5.1. It has been suggested that the length of time an object stays immersed in the BTA solution can affect the efficiency and it might be better to immerse objects for a minimum time (e.g. 15'). The concentrations tested were 0.25M as the closest to the standard 3% w/v and also a lower value of 0.1M. The solvent used was ethanol (analar grade). After the treatment the coupons were placed in the chamber at 95±5% RH and 25 °C and monitored at selected time intervals.

Table 5.1. Factors and levels examined in experiment BTA 1.

Factor	Level -	Level +
Time of Immersion	1h	24h
Concentration	0.1M	0.25M

The design is a full 2^2-factorial design with five replicates in each run and is shown in table 5.2. The total number of coupons used in this experiment was 20 (plus 5 untreated coupons as controls which where also used to calculate the inhibitive efficiency).

[2] A typical BTA solution used is 3% w/v in ethanol or IMS and the object gets immersed into the solution from a few hours to three days, usually under vacuum.

Table 5.2. Full 2^2 factorial design with five replicates used of experiment BTA 1 showing the standard order, the run order, the factors examined and the weight change for 24 hours. This is just an example of the experimental designs used.

StdOrder	RunOrder	Concentration	Immersion	Concentration	Immersion	24h
15	1	-1	1	0.1M	24h	0.0058
11	2	-1	1	0.1M	24h	0.0052
12	3	1	1	0.25M	24h	0.0037
3	4	-1	1	0.1M	24h	0.0060
14	5	1	-1	0.25M	1h	0.0033
8	6	1	1	0.25M	24h	0.0044
6	7	1	-1	0.25M	1h	0.0031
2	8	1	-1	0.25M	1h	0.0029
20	9	1	1	0.25M	24h	0.0053
10	10	1	-1	0.25M	1h	0.0034
9	11	-1	-1	0.1M	1h	0.0042
7	12	-1	1	0.1M	24h	0.0065
5	13	-1	-1	0.1M	1h	0.0041
4	14	1	1	0.25M	24h	0.0048
19	15	-1	1	0.1M	24h	0.0052
16	16	1	1	0.25M	24h	0.0044
13	17	-1	-1	0.1M	1h	0.0039
1	18	-1	-1	0.1M	1h	0.0034
18	19	1	-1	0.25M	1h	0.0037
17	20	-1	-1	0.1M	1h	0.0045

5.3.1.1 Colour changes of BTA 1

Discolouration of the surface was observed in all treated coupons. Although the solutions were initially clear, after the immersion of the coupons, they turned green showing diffusion of copper ions into the solution.

Figure 5.1. Untreated corroded copper coupon and coupons treated with 0.1M, 0.25M BTA for 1 and 24 hours.

The degree of colour change was directly dependant on the concentration and the length of immersion. The changes were greater on coupons treated at the higher concentration and

for longer periods of immersion. The coupons treated with BTA 0.1M/EtOH for one hour presented comparatively the smallest colour changes whilst the ones treated with 0.25M/EtOH had the greatest colour changes. The colour changes are shown in Table 5.3 and in figure 5.1.

Table 5.3. Colour changes of the corroded coupons treated with BTA solutions.

Treatment	Solution (after treatment)	Coupon
BTA 0.1M/H_2O, 1h	Clear, with some loose green sediment in the solution	There are no great changes, except for some green spots
BTA 0.1M/ H_2O, 24h	Clear, with some loose green sediment	The coupon has some green areas
BTA 0.1M/EtOH, 1h	Green, with green sediment	Brown and partly green
BTA 0.1M/EtOH, 24h	Green, with green sediment	Brown (darker) and green
BTA 0.25M/EtOH, 1h	Green opaque, with some green sediment	Brown background and green sediment
BTA 0.25M/EtOH, 24h	Green opaque, with green sediment	Brown background covered with green sediment and some yellowish BTA crystals

5.3.1.2 Results of BTA 1

The results showed that the time of immersion does affect the BTA efficiency. As can be seen from table 5.4, inhibitive efficiency (IE %) drops in the event of a 24h period of immersion. Higher BTA concentration increases the efficiency of the treatment, consequently 0.25M was found more effective than 0.1M. The average IE% in the case of 1-hour immersion at 0.25M was 60% after 24 hours of exposure and dropped to 35% after 35 days, whilst for 24 hours of immersion the efficiency percentages were 44% and 18% respectively. In case of 0.1M for 1hour immersion the efficiency was 50% after 24 hours of exposure and 28% after 35 days, whilst for 24-hour immersion the efficiency percentages were 34% and 10.1% respectively. As can be seen from these results, in both BTA solutions tested, the effectiveness of the treatments was reduced when the coupons remained immersed longer in the solutions (see Appendix 1, BTA1).

Table 5.4. Average values of Inhibitive Efficiency % after 24, 48, 168, 504 and 840 hours of exposure to 95% RH and 25 °C.

BTA 1	Inhibitive Efficiency % (average)				
TREATMENT	24h	48h	168h	504h	840h
BTA 0.1M/EtOH, 1h	50.9	46.4	36.3	30.7	28.2
BTA 0.1M/EtOH, 24h	34.0	28.2	17.1	13.0	10.1
BTA 0.25M/EtOH, 1h	60.7	54.8	42.9	37.7	34.9
BTA 0.25M/EtOH, 24h	44.4	35.8	23.3	20.6	17.7

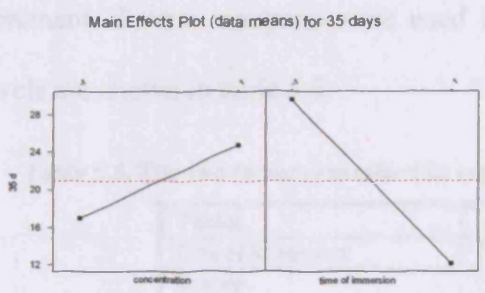
The time of immersion has the biggest influence on the effectiveness. Increase in time of immersion of a treatment causes a considerable decrease in its efficiency. Conversely, the efficiency increases with increased concentration however, the effect of the change was not found to be substantial. The effect of the time of immersion can be seen by the higher effectiveness of 0.1M BTA/EtOH immersed for an hour compared to that of 0.25M BTA when immersed for twenty four hours. Higher inhibitor concentrations ordinarily increase the efficiency of the treatment, however, prolonged periods of immersion might jeopardise this effect.

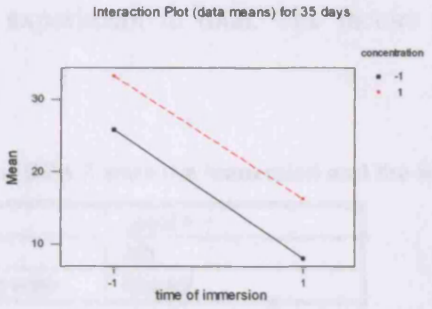
5.3.1.3 Statistical analysis of BTA 1

The exposure of the treated coupons in high relative humidity allowed the evaluation of the treatments using weight change as a measure of the efficiency. The statistical analyses of the experiment included the analysis of the factorial design used, factorial plots, and analysis of variance.

The results showed that both concentration and time length of immersion are important factors. The length of immersion has the greater effect on the outcome (graph 5.1). The concentration factor becomes more significant over time. It is very clear that the inhibitive

efficiency drops dramatically when the objects remain immersed into the solution for longer time periods. The interaction plot showed there is no significant interaction between the factors (graph 5.2).





Graph 5-1. Main effects plot showing that the change of 0.1M to 0.25M increases the efficiency of the treatment, while the increase in time of immersion causes a dramatic decrease.

Graph 5-2. Interaction plot for the tested factors. There is no interaction between concentration and time of immersion. This is shown from the fact that the lines do not meet (they are almost parallel).

5.3.2 Experiment BTA 2

Experiment 1 showed that the time of immersion plays a very significant role in the degree of corrosion protection BTA provides. The second experiment examined the effect the solvent used has on the effectiveness of BTA, in combination with the length of time of immersion. The aim of this experiment was not only to examine whether the solvent used in a solution affects the efficiency of the treatment but also to examine whether this effect changes depending on the time of immersion. Also investigated was the extent to which these factors interact to promote or hinder the inhibitive action.

The concentration used was 0.1M for all solutions; this was selected because BTA is not easily dissolved in water in higher concentrations. Ethanol, IMS and combination of water and ethanol (1:1) have all been used as solvents for BTA (Wharton, G, 2000, personal

communication). Although, ethanol is considered a better solvent for BTA, because of its high cost conservators often opt for less expensive solvents such as those aforementioned. The experimental design is similarly a 2^2 full factorial design with five replicates for each treatment. Twenty coupons were used in the experiment in total. The factors and their levels are shown in table 5.5.

Table 5.5. The two factors examined in experiment BTA 2 were the immersion and the solvent.

Factor	Level -	Level +
Time of Immersion	1h	24h
Solvent	Deionised water	Ethanol

5.3.2.1 Colour changes of BTA 2

The BTA solutions remained clear except for some green sediment observed. There was less sediment in the case of one-hour immersion and more for the solution of twenty four hours. The coupons treated with BTA in de-ionised water had almost no colour change. The coupons immersed only for an hour in the aqueous solution maintained the red colour of the cuprite that they had before the treatment with the exception of some minor green spots, which formed during drying.

5.3.2.2 Results of BTA 2

The most successful treatment was the one where ethanol was used as a solvent and the coupons were immersed in the BTA solution for an hour. The effectiveness of the treatment dropped by almost 50% when the coupons remained immersed for twenty four hours contrary to the general belief that longer immersion results in better inhibition.

Table 5.6. Average values of efficiency of 0.1M BTA in ethanol and deionised water applied on corroded coupons for 1 and 24 hours of immersion.

BTA 2	Inhibitive Efficiency % (Average Values)				
Treatment	24h	48h	168h	504h	840h
BTA 0.1M/H2O, 1h	53.8	34.5	30.8	33.3	25.4
BTA 0.1M/H2O, 24h	-11.0	-19.0	-19.9	-14.8	-12.1
BTA 0.1M/EtOH, 1h	61.7	44.9	35.4	29.3	25.8
BTA 0.1M/EtOH, 24h	40.0	23.8	16.8	10.5	8.0

The effect the length of immersion had on the effectiveness of a treatment was more clearly demonstrated on the coupons treated with the same BTA concentration in deionised water instead of ethanol. Water is generally avoided in conservation of heavily corroded artefacts as it can renew the corrosion processes. The results showed that the use of water as a solvent can indeed accelerate rather than inhibit the corrosion if the coupons stay immersed in the solution for longer periods of time (in this case twenty four hours). However, this was not the case in all the water-based treatments tested, the solution of 0.1M BTA in deionised water for one hour immersion provided satisfactory protection. The efficiency was lower than that provided when ethanol used as solvent for one hour, nevertheless it was higher than the efficiency of BTA 0.1M in ethanol when immersed for 24 hours (see average inhibitive values in table 5.6).

5.3.2.3 Statistical analysis of BTA 2

From the results it is obvious that the factor with the greater influence on the effectiveness of a treatment is the length of time of immersion. Similarly to the results of the previous experiment (experiment 1), an increase in time of immersion caused a decrease in the treatment efficiency. The choice of solvent, although found to be significant at 24 hours, became less significant with time as shown at the main effect plots of 24 and 840 hours of

exposure. There was some no great interaction between the two. The results were fairly consistent throughout the exposure to high RH, even though the effect was greater after 24 hours of immersion (see Appendix 1, BTA2).

In conclusion, the inhibitive efficiency of BTA was best when ethanol was used and the time of immersion was one hour, followed BTA in water for one hour of immersion followed by ethanol treated for 24 hours. The treatment of BTA in water, immersed for 24 hours resulted in acceleration of corrosion. This is related to the pH of the solution which dropped to 3.5 after 24 hours of immersion. The acidity of the solution may have prevented the formation of a protective copper-BTA complex by breaking up the film formed. The pH measurements of aqueous BTA solutions are presented and discussed later in this chapter.

5.3.3. Experiment BTA 3

The third experiment aimed to evaluate whether lower concentrations of BTA could be effective for the inhibition of corroded copper. The general belief is that corroded metals need higher concentrations of inhibitive compounds than corrosion-free metals (Sastri, 1998). However, there have been no studies to establish the optimum BTA concentration required for the inhibition of corroded copper and/or copper alloys. Ammeloot *et al* (1997: 3565-3574) examined the efficiency of different BTA concentrations on copper surface covered with cuprous oxide (Cu_2O) with 0.1M and 0.01M being most effective. Although the artificially corroded coupons used in these experiments were not covered with a single corrosion product (i.e. cuprite) but with nantokite and cuprite, their results were interesting enough to include these concentrations for the purpose of this study.

The second factor examined in this experiment was the solvent. Deionised water and ethanol were used. The levels of the two factors are shown in table 5.7. Both of the concentrations tested were lower than those routinely used in conservation. From the previous experiments it is obvious that both concentration and solvent affect the efficiency of BTA, however since the time of immersion was proved to be more significant for the process, it was imperative to check how these two factors affect the procedure and to examine possible interactions between them. All the coupons were immersed in the inhibitor solutions for 24 hours.

The experiment was a 2^2 full factorial design with three replicates and the total number of coupons used was 12.

Table 5.7. The factors examined in Experiment BTA 3 were concentration and solvent.

Factor	Level -	Level +
Concentration	0.01M	0.1M
Solvent	Water	Ethanol

5.3.2.4 Colour changes of BTA 3

The solutions were clear with only a little green sediment. No great colour changes were observed on the coupons which retained the red colouration of the cuprite. Some green spots were observed on the coupons treated with 0.1M which probably formed during drying of the coupons.

5.3.2.5 Results of BTA 3

In general the results of the lower concentrations were not always consistent. The weight uptake of the coupons treated with 0.1M in ethanol and 0.1M in deionised water were in

agreement with the results of experiment 1. However, the weight changes of the coupons treated with 0.01M in deionised water were largely inconsistent. The initial weight uptake was very low with a bigger disparity in the measurements during monitoring. The most effective treatment overall was that of 0.1M in ethanol as it can be seen in table 5.8. The treatment using 0.1M in water, in agreement with the results of experiment 2, caused acceleration of corrosion with the exception of the third coupon. For this coupon, the efficiency was around 46% after twenty four hours of exposure and dropped to 28% after 840 hours of exposure. However, this could be considered an anomaly especially since the results of coupons treated in other experiments with the same treatment were in agreement with the other measurements.

Table 5.8. Average values of efficiency % of 0.1M and 0.01M BTA in ethanol and water. The range of values was very high in some of these treatments.

BTA 3	Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h
0.01M/H2O	48.5	14.5	6.6	6.2	2.1
0.01M/EtOH	-16.0	-8.8	-14.3	-7.6	-5.9
0.1M/H2O	1.3	5.2	2.7	5.1	4.9
0.1M/EtOH	16.0	14.9	13.4	9.4	8.6

The treatment using 0.01M in ethanol appears to increase the corrosion rate, whilst the same concentration in deionised water proved to be inhibitive. However, the results of the inhibitive efficiency on the three coupons treated with 0.01M in deionised water are also spread and for this reason the results can be considered ambivalent. Nevertheless, this diversity, which could be due to human error during the experimental procedure, shows that it is possible that lower concentration of BTA could be utilised in the future. The outcome of a treatment incorporates many interrelated factors which should be taken into account. One of these, the length of time of immersion, which is in this case twenty four hours,

needs to be further examined in relation to these concentrations.

5.3.2.6 Statistical analysis of BTA 3

At 24 hours of exposure the solvent has the biggest effect on the process whilst the concentration appears to play a very small part. The results change after 48 hours with both factors being significant for the process. The change from ethanol to water has a negative effect in the inhibitive efficiency, especially when a lower concentration of BTA is used, as a result of the interaction between the two factors. However because of the diversity of the weight changes, this result can not be considered conclusive and cannot be taken into account.

Although the concentration of the solution does not affect the efficiency in the first twenty four hours of exposure, it becomes more and more significant with time and after 840 hours is the most significant factor of the two with the higher concentration being more effective than the lower.

In this experiment, the interaction between the two factors (concentration and solvent) is shown to be the most influential for the effectiveness of the treatment. The previous result showed that although the most successful treatment was that of 0.1M in ethanol, in lower concentrations the use of deionised water appears to be more effective than ethanol. Since ethanol is generally considered a better solvent than water for the treatment of corroded copper (as it has been also seen from the previous experiment) this unexpected result clearly demonstrates how significant this interaction could be. The pareto charts show that the interaction between the factors plays the most significant role followed by the

concentration. The only exception to the results is that at 840 hours of exposure, the concentration becomes more significant. The sequence of importance of the factors in this experiment was found to be at twenty four hours interaction between concentration and solvent followed by solvent, followed by concentration. At 48, 168 and 504 hours the sequence changed to interaction between the two factors, followed by concentration, followed by immersion whilst at 840 hours, the concentration became the most significant factor, followed by the interaction between the two factors and finally the solvent.

A lower BTA concentration was not expected to be effective on corroded copper as the presence of corrosion products and the restricted access of the inhibitor to the metal should require higher BTA concentrations. Nevertheless, the BTA concentration used in conservation seems arbitrary and not clearly based on any experimental and/or scientific work. The optimum range of BTA concentrations is yet to be defined and more studies should take place.

5.3.3 Experiment BTA 4

Relative humidity (RH) is known to have a considerable effect on the corrosion of copper. In particular, high relative humidity promotes corrosion. The previous experiments showed that both the concentration and the length of time of immersion are very important for the inhibitive efficiency of BTA. This experiment aimed to examine how the concentration, the immersion time and the relative humidity interact and, consequently, how their interaction affects BTA performance. Table 5.9 shows the factors examined in this experiment. The coupons were exposed after application of inhibitive treatment to 95% RH and to 60% RH.

The first is the value used for assessing the majority of the treatments in this thesis, whilst the latter is a value representing typical RH levels. The concentration and time of immersion used were the same as those examined in the first experiment. The total number of coupons used was 24 (three replicates for each treatment).

Table 5.9. BTA 4 examined 3 factors, concentration, time of immersion and RH.

Factor	Level -	Level +
Concentration	0.1M	0.25M
Time of Immersion	1h	24h
Relative humidity (RH) %	95	60

5.3.3.1 Results of BTA 4

The aim was to understand whether certain treatments that fail to inhibit corrosion in a very aggressive environment can be more effective in less harsh environmental conditions. However, the 840-hour exposure interval was not sufficient to evaluate the effectiveness of the inhibitors at 60% RH. No great weight changes were observed on all coupons, including the untreated control coupons. Longer periods of exposure to 60% would have been required to examine the behaviour of the coupons, this was not possible due to time restrictions and other research priorities related to the synergism between inhibitors. The experiment aimed to compare the treatment behaviour at 95 and 60% RH, however the coupons exposed at 95% RH were flaking corrosion after thirty five days of exposure, making it difficult to continue their weight based evaluation. Further exposure of only part of the test (in this case of the coupons exposed to 60% RH) was out of the scope of this experiment.

Table 5.10. Average values of inhibitive efficiency of experiment 4.

BTA 4	Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h
BTA 0.1M/EtOH, 1h, 95% RH	24.1	19.9	11.7	11.3
BTA 0.1M/EtOH, 1h, 60% RH	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 95% RH	19.7	14.5	10.1	3.2
BTA 0.1M/EtOH, 24h, 60% RH	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 95% RH	36.8	35.0	31.3	23.3
BTA 0.25M/EtOH, 1h, 60% RH	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 95% RH	32.0	26.2	20.6	8.5
BTA 0.1M/EtOH, 24h, 60% RH	100.0	100.0	100.0	100.0

From the results it was found that RH plays a very significant role in the effectiveness of a treatment. Copper corrosion was very slow when exposed to lower RH, whilst in higher RH the corrosion was accelerated. The previously examined factors were less significant compared to the humidity. Yet again higher concentration of BTA and less time of immersion resulted in less weight uptake and therefore better corrosion protection (see table 5.10).

Interaction between concentration and RH appears to be the most important relationship. From the interaction plots the most important factor is the RH, followed by concentration and time of immersion, then interactions between time of immersion and RH, concentration and time of immersion, concentration and RH, and all three factors interacting. Once more, except RH which is the most important factor affecting efficiency, the considerable interactions between factors change over time. For example up to 168 hours of exposure the interaction between concentration and time of immersion is substantial and after 504 hours of exposure it is not any more.

The results of the above experiments showed that there variable such as the length of the time an object stays immersed into a BTA solution affects greatly the film formed and its efficiency. Concentration also affects the effectiveness but to a lesser extent as is the solvent. However, the interaction of certain variables such as the solvent and the time of immersion can result in accelerated corrosion such as the use of water as a solvent for twenty four hours or immersion.

5.3.4 Re-use of BTA solutions

For financial as well as ecological purposes BTA solutions are often used repeatedly for the treatment of several artefacts. The financial reasons are more related to the cost of the solvent, usually ethanol, which is very expensive and less to the cost of BTA. The disposal of BTA and its suspected toxicity is another important factor for the reuse of BTA solutions, especially in countries where disposal of chemicals by specialised companies does not exist. Conservators show discrepancy with the number of times a solution should be used. Often, BTA solutions are used for years either until a green sediment is observed or the solution is not clear anymore. The BTA treatment frequently involves rinsing off the object with ethanol or IMS after the treatment in order to remove any white tide lines formed on the metal surface[3].

A lot of factors could possibly affect the efficiency of BTA using an already used, old solution. One of the most obvious is the pH of the solution. As has already been noted, heavily corroded copper results in a low pH of the BTA solution. The BTA solution can

[3] Sherman, F, 2004, personal communication. British Museum BTA treatment.

become very acidic with time and after repeated uses. The film formation is greatly affected by the pH of the solution. In a low pH, the Cu-BTA complex formed is thicker and less polymerised, therefore less protective (Brusic *et al*, 1991: 2253). One of the biggest problems is that the concentration is not known as part of the solvent evaporates and part of the BTA is bonded to copper. Moreover, since BTA is found as BTAH and BTA^- within the solution, with BTA^- preferably adsorbed into copper to form a complex, after repeated uses of the solution the free BTA^- present becomes difficult to ascertain (Sastri, 1998). This latter phenomenon could be the reason of the failure of BTA treatments.

The repeated uses of the solution in combination with the length of immersion of the object in the solution are interrelated factors and possibly result in less effective treatments. The extent of the effect the used solution has on the effectiveness of BTA is not usually considered. Another issue is whether already used BTA solutions alter the colour of the corrosion products more than a freshly prepared solution.

The following series of experiments examined the degree of corrosion protection offered by previously used solutions. The experiments aimed to examine whether the inhibitive efficiency is affected by these solutions and to what extent. The experiments were performed on artificially corroded coupons.

5.3.5 Experiments BTA 5 and BTA 6

Freshly prepared and already used solutions of BTA in two different concentrations in ethanol were tested at two different immersion times (one hour for experiment 5 and twenty

four hours for experiment 6). The experiments included two factors at two levels with three replicates for each treatment. Twelve coupons were used for each experiment. Table 5.11 shows the levels of the factors tested. The solutions that were used to treat the coupons for the "fresh" solution were used immediately after for the treatment of the second batch of coupons (those treated with used solutions). Because of some solvent evaporation observed after the first application, the glass beakers were filled with ethanol up to 25 ml to keep the same volume. The evaporation of the solvent was naturally greater on the coupons immersed for twenty four hours.

Table 5.11. The same factors and levels were used for experiments 5 and 6, for 1 and 24 hours of immersion respectively.

Factor	Level -	Level +
Concentration	0.1M/EtOH	0.25M/EtOH
Solution	Used	Fresh

5.3.5.1 Colour changes of BTA 5 and BTA 6

Both the 0.1M and 0.25M BTA solutions turned green with green sediment after the first use as observed in the previous experiments with similar BTA solutions. The solutions that were used for 24 hours were opaque with more sediment. The coupons treated with the used solution became darker and a green deposit was found on the surface. White BTA crystals were also formed on some coupons (especially those treated with used solution of BTA 0.25M for 24 hours). The colour changes of the coupons treated with the already used BTA was the greatest. However, except for the colour alteration, the film appeared thicker when examined under stereomicroscope as well as under the SEM (see section on SEM observations).

5.3.5.2 Results of BTA 5

The results of the fifth experiment showed that in general the used solutions resulted in greater weight uptake; subsequently the treatments were less effective than those of the fresh solutions. The inhibitive efficiency in case of 0.1M dropped from 45% to 21% after the twenty four-hour exposure and after 840 hours from 24% to 9.7%. In case of 0.25M, the IE% dropped from 57% to 35% after 24 hours and after 840 hours from 17% to 13%.

Both concentration and solution are important variables for the efficiency of BTA but concentration was found to be the least significant of the two. An increase in concentration causes an increase in efficiency but the re-use of the solutions results in decrease of the efficiency. There is no relationship between the two factors, the effects of each one are independent and therefore changes on one factor do not have an effect on the other.

Table 5.12 shows the values of the inhibitive efficiency values.

Table 5.12. Average inhibitive efficiency values of treatments with re-used BTA solutions, experiments 5 and 6.

	BTA 5 and BTA 6	Inhibitive Efficiency %				
	Treatment	24h	48h	168h	504h	840h
Experiment 5, 1h	BTA 0.1M, fresh	48.5	45.9	34.1	29.8	26.9
	BTA 0.1M, used	20.0	19.4	10.4	12.6	8.7
	BTA 0.25M, fresh	61.0	55.0	43.3	39.7	36.2
	BTA 0.25M, used	34.1	28.0	16.1	14.3	12.3
Experiment 6, 24h	BTA 0.1M, fresh	28.2	23.7	15.3	11.4	8.9
	BTA 0.1M, used	39.3	38.6	27.5	26.7	24.4
	BTA 0.25M, fresh	43.3	35.4	23.5	20.7	17.5
	BTA 0.25M, used	40.9	41.0	27.1	26.0	24.0

5.3.5.3 Results of BTA 6

The outcome of the sixth experiment (24 hours of immersion) presented very interesting results. Initially, after 24 hours of exposure, the used solution was found to be less effective than the fresh solution. However, even though the used solution of 0.25M caused an increase in weight uptake and a decrease in the effectiveness of the treatment for the first 24 hours of exposure, the efficiency of the used solution proved to be slightly higher than that of the fresh solution after 48 hours. In case of the 0.1M solution, the reuse of the solution resulted in less weight uptake and, subsequently an increase in efficiency. Two out of the three coupons treated presented increased inhibitive efficiency; the third coupon had inhibitive efficiency close to that of the treatment using a fresh solution for 24 hours. It was clear that the coupons treated with re-used solutions showed higher IE% than those treated with new solutions in the long term exposure. This result was unpredicted, especially since experiment 5 showed that the re-use of the BTA solution results in drop in the overall efficiency.

The analysis of the experiment showed that contrary to experiment 5, in this case both factors are significant, with the concentration being more important as a variable for the efficiency than the used solution. For example after 24-hour exposure, the choice of solution (fresh or not) used was totally insignificant for the process. The change from fresh to used solution caused a drop in the inhibitive efficiency in the first 24 hours, result that was reversed after 48 hours of exposure where the used solution resulted in increased efficiency. The degree of significance for the two factors changed over time. However, primarily, the concentration was the variable that was found to be more important. There

was little interaction between the two factors. The next two experiments and the analysis may shed some light to the reason for this outcome.

5.3.6 Experiments BTA 7 and BTA 8

Similarly to the previous series, experiments 7 and 8 aimed to examine the effect re-used solutions have on the IE. In these experiments, the re-use of BTA was examined in combination with different solvents (i.e. deionised water and ethanol). 2^2 full factorial experiments with three replicates were used. The concentration used was 0.1M. Table 5.13 shows the factors and the levels tested in these experiments. In experiment 7 the coupons stayed immersed within the solutions for an hour and in experiment 8 for 24 hours.

Table 5.13. Factors examined at BTA 7 and BTA 8 experiment. In BTA 7 the immersion time was 1 hour and in BTA 8, 24 hours.

Factor	Level -	Level +
Solvent	Deionised water	Ethanol
Solution	Used	Fresh

5.3.6.1 Colour changes of BTA 7 and BTA 8

The coupons treated with 0.1 M BTA in aqueous solutions did not show great colour changes, especially after 1 hour of immersion the coupons retained the colour of red cuprite. The aqueous solutions were clear with some loose green sediment after 1 hour of immersion. The used solution presented more green sediment after the immersion of the coupon. The 0.1M in ethanol solutions were green with a green sediment and the used solution became opaque with time.

After 24 hours of immersion the coupons exhibited some green surface deposits on the lower part of the coupons. The coupons treated with used 0.1M BTA in ethanol showed

more green deposits on the surface and darkening of the cuprite layer.

5.3.6.2 Results of BTA 7

In experiment 7, the results were similar to those of experiment 5. The used solution caused a significant drop in the effectiveness of the inhibitor. The efficiency of 0.1M BTA in water dropped from 38% to -3% after 24 hours of exposure and in case of 0.1M in ethanol, the efficiency dropped from 46% to 21%. As it can be seen in table 5.14 the decrease in efficiency was consistent throughout the 840 hours of exposure. Although ethanol was proved to be a better solvent on the whole, the solvent as a factor is not as important for the process as is the re-use factor. The type of solution played the most important role for the effectiveness of the treatment. There was also interaction between the factors which was remarkably evident after the first twenty four hours of exposure.

Table 5.14. Average inhibitive efficiency values of treatments with re-used BTA solutions examined in BTA 7 and BTA 8.

	BTA 7 and BTA 8	Inhibitive Efficiency %				
	Treatment	24h	48h	168h	504h	840h
Experiment 7, 1h	0.1M/H2O, fresh	44.4	42.4	36.8	34.7	32.3
	0.1M/H2O, re-used	-5.1	-2.5	-5.2	2.2	32.3
	0.1M/EtOH, fresh	48.5	45.9	34.1	29.8	32.3
	0.1M/EtOH, re-used	19.9	19.4	10.4	12.6	32.3
Experiment 8, 24h	0.1M/H2O, fresh	-22.4	-18.2	-20.0	-14.9	-12.4
	0.1M/H2O, re-used	15.9	18.1	15.6	16.4	16.7
	0.1M/EtOH, fresh	37.3	30.5	18.9	14.2	10.9
	0.1M/EtOH, re-used	36.0	39.1	25.8	20.5	20.9

5.3.6.3 Results of BTA 8

The results of the experiment at twenty four hours of immersion were similar to those of experiment 6. The inhibitive efficiency appears to increase in the case of used solutions.

Interestingly, although the corrosion of the coupons treated with 0.1M in deionised water for 24 hours was accelerated, the coupons treated with a used solution exhibited IE of 17% throughout the 840 hours of exposure. Another interesting outcome was that the weight uptake was less than that observed in other BTA treatment therefore, instead of increasing resulting in higher IE at 48 hours than at 24 hours. This result could be explained as an experimental error that occurring during weighing. Another explanation can be that the corrosion of the coupons flaked off during transport, resulting in lower weight. Similar results were observed in the case of 0.1M in ethanol. The used solution provided higher protection than that of the fresh solution.

The statistical analysis of the experiment showed that for the first 168 hours, the solvent was the most important factor in the inhibition process. Changing of the solvent from water to ethanol caused a big increase in the efficiency of BTA. The freshness of the solution used became significant after 168 hours and ended up being more important than the solvent at 840 hours. However, in case of the type of solution used, the change from level -1 to 1 had the reverse effect in the overall process, with the used solution increasing the efficiency of the treatment.

Although the results were very different to that expected, as the same overall outcome was observed in two experiments (6 and 8) and both times on coupons treated with solutions for 24 hours (in the case of used solutions it was treatment with solution used for a further 24 hours in another treatment) they appear to be a definite pattern. Why the 24-hour treatment proved to be less effective whilst the same treatment with solution that has been used

previously to treat other coupons, when used for a further 24 hours, provided increased protection is yet to be answered. A possible explanation is that the re-used BTA solutions had dissolved copper ions from the previous treatment. The used solutions in all cases (especially those of the 0.25M and 0.1M in ethanol) were not translucent anymore but opaque green with green sediment. The new coupons were immersed within the same beaker and the sediment remained. One of the reported ways that BTA acts on copper is that of copper-BTA film formation on the surface following a copper dissolution mechanism. The used solutions had a lot of dissolved copper from the previous coupons, as it is indicated by their colour. The amount of copper dissolved cannot be measured easily therefore, this can only be a theory that needs further research. Faltermeier (1995) examined the dissolution of metallic copper, cuprite, malachite and nantokite powders caused by BTA using AAS (Atomic Absorption Spectroscopy). He found that BTA caused no dissolution to metallic copper, little dissolution of cuprite and malachite and partial dissolution of nantokite. He suggested that except nantokite there was no significant dissolution of copper compounds caused by BTA (Faltermeier, 1995: 230-235). The coupons used for these experiments were covered with nantokite and cuprite, so some dissolution of nantokite which also caused the discoloration of the solution was accepted based on the aforementioned measurements.

What may have happened and caused the increased inhibitive efficiency is that since the solution was saturated with copper ions (sediment) it was not able to dissolve more copper from the coupon, therefore the inhibition was faster and more effective. This would be either because of the precipitation of the pre-existing copper BTA complex found in the

solution or because of a much more straight forward chemisorption of free BTA in the solution. These experimental results, although surprising, might help in a better understanding of the way in which BTA works and the reasons for its failure.

5.3.7 Weight changes of coupons after BTA treatments

Most of the coupons presented a slight weight uptake after the inhibition treatment. The weight gained is indicative of the BTA-Cu complex formed on the surface. The weight measurements showed that the weight gained is dependent on all the factors examined. Concentration of the solution, the solvent and the period the coupon stayed immersed in the solution all affect the weight gained. This finding cannot be used as a measure for the thickness since inhibition is a chemical reaction with the metal, but it is however characteristic of the treatments and worth mentioning. Therefore, it was noted that the coupons treated with 0.1M aqueous solutions of BTA gained less than 0.001% of their weight after one hour of treatment and around 0.03% after twenty four hours of immersion. In case of 0.1M BTA in ethanol, the coupons treated at one hour of immersion gained around 0.025% and 0.045% after twenty four hours of immersion.

Interestingly, the coupons treated with 0.25M BTA in ethanol gained the same weight at both periods of immersion that was between 0.04 to 0.006%.

The re-use of the solutions resulted in a different picture. In some cases the amount of weight gained remained in the same levels as those of the single solutions (e.g. 0.1M BTA in deionised water) whilst in other there was a dramatic change in the weight. Coupons

treated with re-used solutions of 0.1M in ethanol showed less weight uptake (0.01-0.02%) than that observed in those treated with freshly prepared solutions. There was also a case of weight loss.

Re-used solutions of 0.25M BTA in ethanol had weight uptake that were in some cases less than those observed in coupons treated with fresh solutions, or more and there were also cases where the coupons lost weight (in particular when the solutions was previously used for twenty four hours). Thus, although the weight uptake of corroded coupons treated with fresh BTA solutions are consistent, the weight uptake/loss of the coupons treated with solutions that have already been used previously indicates that there is no homogeneous mode of film formation in the latter case partly suggesting the BTA failure observed in the experiments.

5.3.8 Discussion of results of artificially corroded copper

The results of the experiments showed that inhibitive efficiency is greatly affected by the length of time of immersion, the concentration, and the solvent used. In most experiments the factors were interrelated. Their interaction caused both positive and negative effects on the treatments and their efficiency. From the factors tested, the length of time of immersion was found to be the most important. The negative effect of the long immersion time was noted by Faltermeier (1995) and Brusic *et al* (1991) who suggested that the reason for the BTA failure might be related to pH drop and that shorter immersion of an object in the BTA solution might be better over longer ones (Faltermeier, 1995, Brusic *et al* 1991). The concentration of the solution is another issue examined in these experiments. The

customary use of 3% in ethanol has not really been questioned even though the choice is not based on scientific research. More experiments with different concentrations are required in order to establish the optimum concentration range BTA is mostly effective at. One of the questions arising from the results is how BTA can be effective in relatively low concentrations (e.g. 0.005M) less effective in slightly higher concentration (0.01M) and more effective in even higher concentrations (0.1 and 0.25M). The use of artificially corroded coupons helped to limit the number of parameters to be taken into account when examining what might affect the inhibitive efficiency provided by BTA, however, it was clear from the experimental results that the interaction between different factors play in some cases an equally important role. The experiments were used to identify the patterns observed in the efficiency of a treatment when changing different parameters and the analysis could possibly shed light to the reasons behind the results.

5.3.9 pH of BTA solutions

The pH of the BTA solution has been reported to drop significantly during use. Since pH is thought to be related to the BTA failure to inhibit corrosion of heavily corroded copper, it was essential to measure the pH of the aqueous BTA solutions. 0.1M BTA in deionised water is slightly acidic and it drops from 5.8 to 4.2 after one hour of immersion of the coupon, and to 3.5 after 24 hours of immersion. These measurements are just an indication of the reactions taken place within the BTA solution. The pH drop after immersion of the copper coupons might explain the experimental results.

The results showed that the time of immersion had a great influence on the effectiveness of

a treatment. In all solutions tested, the longer the period of immersion the less effective the treatments. The extended immersion of the corroded copper coupons within the solution caused some dissolution of copper ions which in turn resulted in lower pH. Interestingly, there was no significant change of the pH when clean copper was immersed. This outcome is related to the presence of nantokite found underneath cuprite of artificially corroded copper coupons. Nantokite causes a significant drop in pH. Faltermeier (1995) reported that the pH of nantokite immersed into BTA solution for twenty four hours was found to be as low as 1.4 (Faltermeier, 1995: 222).

Table 5.15. pH values of aqueous BTA solutions.

Solution	pH	Colour of solution
BTA 0.1M, pure	5.8-5.5	Clear
BTA 0.1M, 1h	4.1-4.2	Clear, green sediment
BTA 0.1M, 24h	3.5-3.6	Clear, green sediment
BTA 0.1M, 1h/1h	4.1-4.0	Clear, green sediment
BTA 0.1M, 1h/24h	3.5	Slightly green, green sediment
BTA 0.1M, 24h/1h	3.7	Slightly green, green sediment
BTA 0.1M, 24h/24h	3.2	Slightly opaque green, green sediment
BTA 0.01M [4]	5-5.1	Clear
BTA 0.01M, 1h	3.6-3.7	Clear, a little green sediment at the bottom of the beaker
BTA 0.01M, 24h	2.75-2.8	Opaque/ light green

The pH values of the BTA solutions are presented in table 5.15. A low concentration BTA solution (0.01M) becomes very acidic after immersion of the copper coupon for 24 hours (pH≈2.8). In general the pH values of the 0.01M solutions were lower than those of 0.1M. The pH of 0.01M BTA drops dramatically after 24 hours of immersion. A low pH such as this could result in breakage of any protective layers formed in the meantime, causing

[4] Roberts (1974) found the pH of the aqueous solution of 0.017M to be 5.25 at 60°C (Roberts, 1974: 273).

failure of the treatment. This could possibly explain the results of experiment 3.

The pH of the re-used solutions also dropped slightly over time. In case of 0.1M in deionised water for an hour the pH remained the same after the immersion of the second coupon but dropped from 3.6 to 3.2 after a further 24 hour immersion. It is evident from the results that longer immersion results in lower pH.

5.4 Uncorroded copper coupons

Another set of similar experiments took place on clean copper coupons since the type and extent of corrosion present could affect the efficiency of an inhibitor. The clean copper coupons were air abraded, degreased, dried, weighed and then treated with BTA. Unfortunately, it was not possible to draw conclusions about the BTA efficiency on clean copper because the 35-day exposure to high RH was not sufficient alone to induce corrosion. More rigorous tests were required or longer periods of exposure to high relative humidity. Copper is highly resistant to corrosion as can be seen from the EMF series (see Chapter 2). The evaluation of the inhibitor was based on the weight uptake. Most of the coupons lost weight during the first days. This was probably due to the fact that BTA is volatile and part of it evaporated. Although the inhibitive efficiency of BTA on clean copper could not be assessed with a simple high RH test, observations from these experiments are discussed, as it is very important to illustrate the difference between metallic and corroded copper. The results of the clean coupons showed that the substrate does affect the Cu-BTA film formation. The analyses of the uncorroded copper are presented along with the analyses of the corroded treated coupons for comparative purposes.

Even if there were no such changes in weight uptake as to allow evaluation of the inhibitive efficiency of the treated coupons, there were many differences in terms of the film formation, which inevitably affected the appearance of the coupons. The copper surface appeared darker after the BTA treatment. These colour changes are discussed here and the film formation was extensively investigated through analytical techniques and are discussed in detail later on this chapter.

Coupons treated with 0.01M in water and in ethanol did not show any surface alterations. The coupons kept their metallic appearance. The presence of the film is not even evident in case of 0.01M/water. 0.01M in ethanol caused a very slight darkening (not evident with naked eye) on the surface. Upon exposure to high RH there were no alterations of the surface. The untreated copper coupons lost their metallic shine after the exposure, but not the treated coupons.

5.4.1 Colour changes of clean copper treated with BTA

These experiments aimed to examine factors affecting the BTA efficiency. The coupons were treated with different BTA solutions and then exposed at 25°C to either 95±5 % or 60±5% RH. The colour changes induced as the metallic copper are presented below. The results are presented according to the treatment and other relevant information shown in table 5.16.

5.4.1.1 0.1M BTA/H2O

In both groups of coupons treated with 0.1M BTA in H_2O for one and for 24 hours, white inhibitor residues were observed on the surface after drying of the coupons. These were crystals of BTA formed because of the evaporation of the solvent. No changes were found after the exposure to high RH and the coupons kept their metallic appearance.

5.4.1.2 0.1M BTA /EtOH

The coupons treated with 0.1M BTA/EtOH for an hour resulted in slightly duller surfaces than before treatment. The film is not uniform and there were BTA residues. After the exposure to high RH the coupons got darker probably due to the oxidation of the surface. The untreated coupons appeared a lot darker than those that were treated as BTA partly prevented the oxidation of the metal.

The coupons treated with the same solution for 24 hours had a more uniform and slightly darker surface with BTA residues than those treated for an hour. Also, there were white BTA residues and a few green/black areas on the surface. After exposure to high RH the surface became slightly darker, but again not as much as on the untreated coupons. In both cases the coupons kept their metallic appearance although they became slightly darker.

5.4.1.3 0.25M BTA /EtOH

Similarly, all 5 coupons treated with 0.25M BTA in ethanol had a non-uniform darker metallic surface. After exposure to high RH the metal surface got darker. There were also a few dark spots on the surface of the coupon immersed for 24 hour with the BTA solution,

which turned green after the exposure to high RH%. The coupons kept their metallic appearance.

Table 5.16. Table showing the effect treatments had on the metallic appearance of clean coupons.

Treatment	Time of immersion	Metallic appearance
BTA 0.1M/H_2O	1h	Yes
BTA 0.1M/H_2O	24h	Yes
BTA 0.1M/EtOH	1h	Yes
BTA 0.1M/EtOH	24h	Yes
BTA 0.25M/EtOH	1h	Yes
BTA 0.25M/EtOH	24h	Yes

5.4.1.4 Comments

The metallic appearance of copper is affected by BTA concentration as well as solution choice. Although the treated coupons presented less oxidation on the surface than the untreated ones, the treatments changed the appearance of the coupons. Both concentration and time of immersion affected the film formation as seen from the pictures, and under the microscope. Visually, the films are not uniform in appearance. There were inhibitor residues and dark spots on coupons exposed to in higher concentration solutions. Coupons treated with 0.25M BTA in ethanol for twenty four hours presented the most colour alterations.

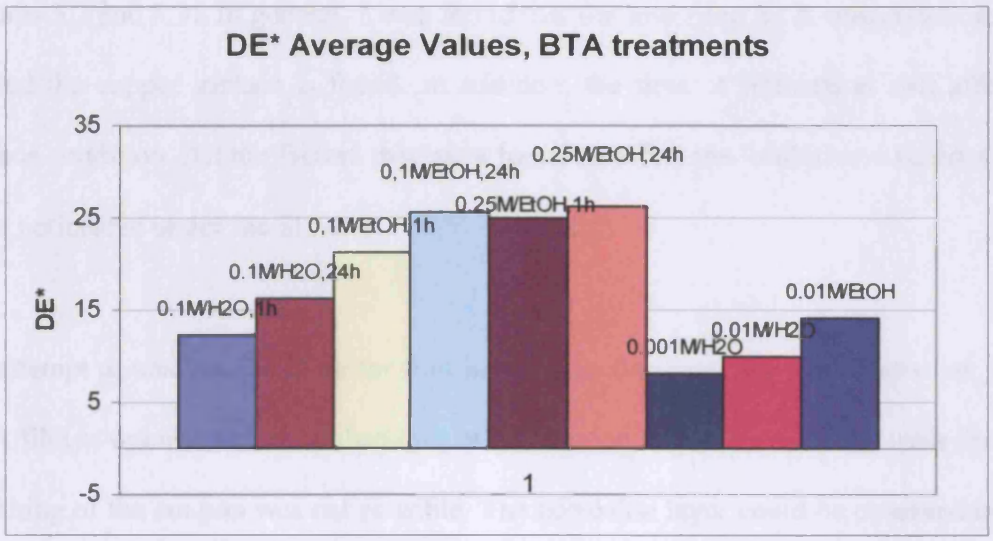
5.5 Colour measurements

The factors examined affected not only the complex between BTA and copper and the efficiency of the treatment but also the colour of the coupon surface. Table 5.17 shows the average ΔL^*, Δa^*, Δb^* and ΔE^* values of all BTA treatments applied on corroded copper examined in this chapter.

Table 5.17. DL*, Da*, Db* and calculated DE values of corroded copper coupons treated with different BTA solutions.

Treatment	ΔL*	Δa*	Δb*	ΔE
BTA 0.1M, H2O, 1h	-9.50	-5.57	-5.46	12.29
BTA 0.1M, H2O, 24h	-8.42	-12.51	-6.29	16.34
BTA 0.1M, H2O, 1/1h	-11.09	-7.32	-9.35	16.24
BTA 0.1M/H2O, 1/24H	-9.78	-11.70	-8.68	17.55
BTA 0.1/H2O, 24/1H	-10.90	-13.93	-12.04	21.39
BTA 0.1M/H2O, 24/24H	-6.26	-13.64	-8.06	17.03
BTA 0.1M/EtOH, 1h	-11.13	-12.41	-13.03	21.16
BTA 0.1M/EtOH, 24h	-8.16	-19.08	-15.05	25.63
BTA 0.1M/EtOH, 1/1h	-12.22	-14.93	-11.00	22.21
BTA 0.1M/EtOH, 1/24h	-10.12	-22.49	-18.37	**30.75**
BTA 0.1M/EtOH, 24/1h	-18.95	-11.75	-7.72	23.60
BTA 0.1M/EtOH, 24/24h	-8.98	-20.96	-19.32	**29.89**
BTA 0.25M 1h	-13.42	-14.97	-14.79	24.96
BTA 0.25 24h	-5.48	-20.95	-14.72	26.18
BTA 0.25 1/1h	3.00	-22.14	-14.87	26.84
BTA 0.25 1/24h	-20.41	-20.83	-13.50	**32.13**
BTA 0.25, 24/1h	3.13	-22.08	-14.72	26.72
BTA 0.25, 24/24h	-7.51	-21.63	-15.86	**27.85**

The ΔE is the difference between a treated coupon and an untreated reference coupon. The higher the ΔE value is, the greater the colour changes. From the ΔE values one can see that all the factors examined affect to a great extent the colour changes. Coupons treated with 0.25M, the longer periods of immersion in the solutions resulted in increased ΔE, therefore greater colour changes. The solvent also affected the surface colouration, as 0.1M in ethanol present different ΔE* value than 0.1M in deionised water. Graph 3 shows the ΔE* values of the main BTA treatments illustrating how important these variables are for the colour of an object. The treatment of coupons using already used solutions also present greater colour changes.



Graph 5-3. DE values of BTA treatments. The higher the DE, the greater the colour change is.

It is worth mentioning that the corroded copper coupons were covered with cuprite so the measurements refer to cuprite only. Different corrosion products will be affected in a different manner, depending on their chemical composition.

5.6 SEM imaging

SEM helped to trace any visual differences at high magnification of BTA films formed on clean and corroded copper coupons. The examination took place under different selected magnifications (400, 1000, and 4000 in all cases and higher magnification for details) for comparative reasons. The observations of both corroded and clean copper coupons treated with different BTA solutions, helped significantly in the understanding of the film formed on the surface. The examination started with untreated copper coupons and continued with those treated with BTA. One of the most interesting features observed was how different solutions followed or not the surface details. This was mostly evident on the corroded copper, where the surface was covered with very distinctive copper oxide crystals (see

Figures 5.2 and 5.3). In general, it was found that the lower the BTA concentration, the less altered the copper surface is found. In addition, the time of immersion also affected the surface condition. All the factors that were found to affect the inhibitive efficiency of BTA were noticeable under the SEM.

An attempt to observe the inhibitor film in cross section was also made, however since the BTA film is organic and no embedding of the coupon was permitted, the cross section and polishing of the coupon was not possible. The corrosion layer could be observed unlike the inhibitor film.[5]

The observations on clean copper did not show any particular interest. There is clearly a film formed on clean copper with 0.25M forming a thicker film on the surface. Benzotriazole solutions were also applied on a glass slide and observed under the SEM, however it was difficult as the electron beam burnt the film.

Coupons treated with the BTA treatments tested in the humid chamber were observed under the SEM.

[5] Tests using resins that could allow observation of the organic film were unsuccessful, so embedding of the coupons was not possible.

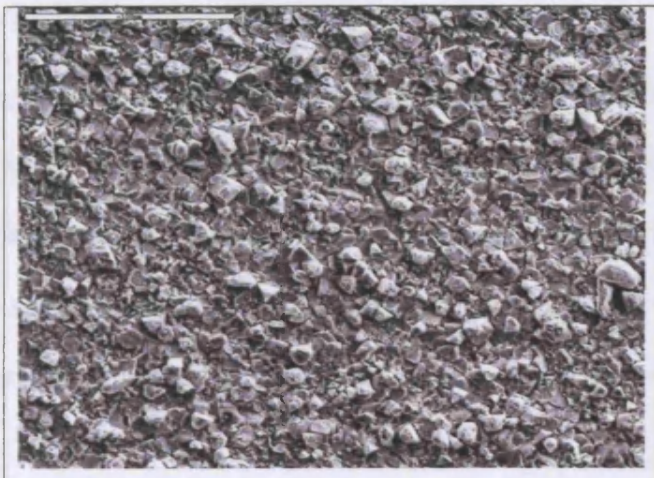


Figure 5.2. SEM photo of artificially corroded copper coupons.

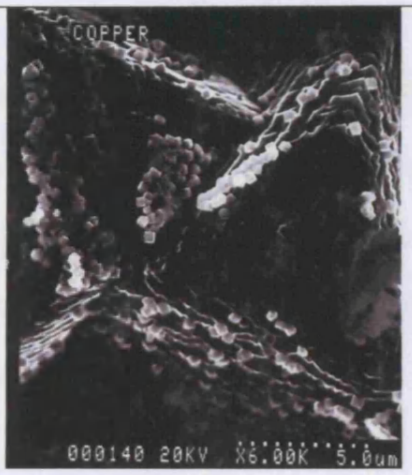


Figure 5.3. SEM detail of cuprite crystals on artificially corroded copper coupons.

5.6.1 SEM observations of corroded copper coupons

The concentrations 0.01M in both ethanol and deionised water did not seem to alter the copper surface. The copper-BTA film presence was directly related to its thickness. In this case, since all of the copper crystals are clearly distinctive, the BTA might be adsorbed on the copper surface, or the film formed was very thin.

Similar observations were made on coupons treated with 0.1M in water for one hour. Coupons treated for 24 hours, presented similar picture with the addition of some BTA crystals and a fluffy precipitant formed in some parts of the surface.

The coupons treated in 0.1M in ethanol for an hour presented a different picture (Fig. 5.4). The surface is covered with a thicker film and the copper crystals are not visible anymore. In addition to what observed after one hour of immersion, at longer periods of time of immersion (24 hours) a dark precipitant was found present on some parts of the surface.

The coupons treated with 0.25M in ethanol for both one and 24 hours showed a similar picture to that of 0.1M in ethanol (Figures 5.3 and 5.4). There is a film around the copper crystals, which however follows the copper crystals. The coupons treated for 24 hours in the solution presented thicker precipitant in some parts of the surface. Table 5.18 shows alteration of the copper surface both macroscopically and under the SEM.

Table 5.18. SEM observation of copper treated with BTA solutions

BTA solution		Description of copper surface after treatment	Definition of copper oxide crystals	Precipitate
1	0.01M/H_2O, 1h	No alteration	Yes	No
2	0.01M/ H_2O, 24h	No alteration	Yes	Some
3	0.01M/EtOH, 1h	No alteration	Yes	No
4	0.01M/EtOH, 24h	No alteration	Yes	No
5	0.1M/H_2O, 1h	No alteration	Yes	No
6	0.1M/ H_2O, 24h	No alteration but with BTA crystals and precipitant present	Yes	Yes, whitish fluffy
7	0.1M/EtOH, 1h	Thin film	Yes	No
8	0.1M/EtOH, 24h	Thin film	Yes	Some, thin dark
9	0.25M/EtOH, 1h	Thick film	Yes	No
10	0.25M/EtOH, 24h	Thick film	Yes	Yes, fluffy whitish
11	0.1M/ H_2O, 1+1h	Thin film	Yes	No
12	0.1M/ H_2O, 24+24h	Thicker film than 8	Yes	Whitish
13	0.1M/EtOH, 1+1h	Thick film	Yes	No
14	0.1M/EtOH, 24+24h	Thick film	Yes	Yes, fluffy whitish
15	0.25M/EtOH, 1+1h	Thick film	Yes	
16	0.25M/EtOH, 24+24h	Thick film, surface covered 50% by precipitant	Yes	Yes, fluffy whitish

The reuse of the solution showed a different picture. The copper surface was covered with thicker films and in most cases there were precipitant and BTA crystals formed on the surface. The differences were not that obvious in case of solutions pre-used for an hour for another treatment, but were more obvious in the coupons treated with solutions where coupons were immersed previously for 24 hours. The definition of the copper crystals was

lost on coupons treated with pre-used solution of 0.1M in water especially those were the solution was re-used for 24 hours and in some cases BTA crystals were formed on the surface (e.g. coupons treated for 24 hours with solution that was already used for a further 24 hours). Similarly, the coupons treated with a re-used solution of 0.1M in ethanol showed thicker film formation on the surface. In particular, the coupons that stayed immersed for 24 hours in solution that had been previously used for 24 hours presented a fluffy whitish precipitant (Fig. 5.7). The surface alteration was more evident in case of re-used solutions of 0.25M in ethanol. The surface was partly covered with whitish precipitant similar to that of 0.1M in ethanol, only larger and thicker in case of coupons treated with solution that was used before for 24 hour immersion of another coupon.

Some coupons were also observed after their 24-hour exposure to 95±5%RH. The active corrosion was not always visible with naked eye. Under the SEM, pustules of active corrosion were observed. These had different sizes and shapes and what was more interesting was that on top of these pustules there was evidently the BTA film, cracked and lifted by the corrosion. This clearly shows there is a very thin film formed on the copper surface (Figures 5.8 and 5.9).

Figure 5.4. Corroded copper treated with 0.1M BTA for 1 hour.

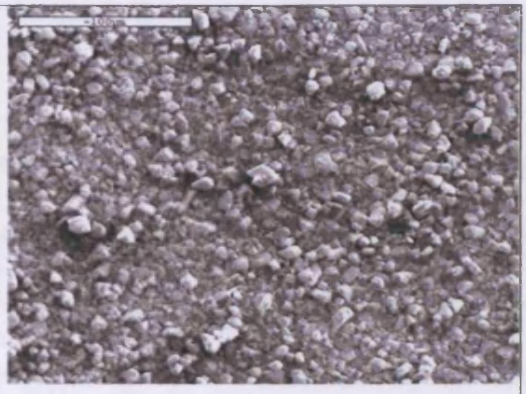


Figure 5.5. Corroded copper treated with 0.25M for 1 hour

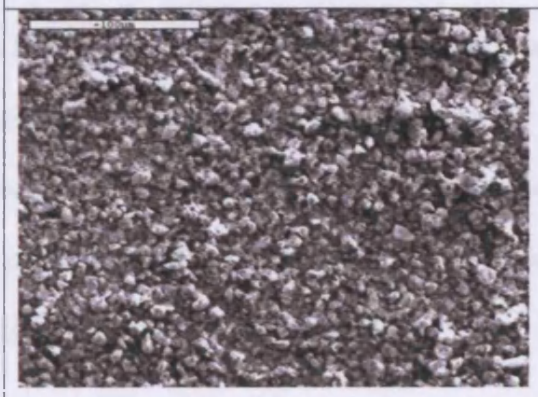


Figure 5.6.Corroded copper treated with 0.25M for 24 hours.

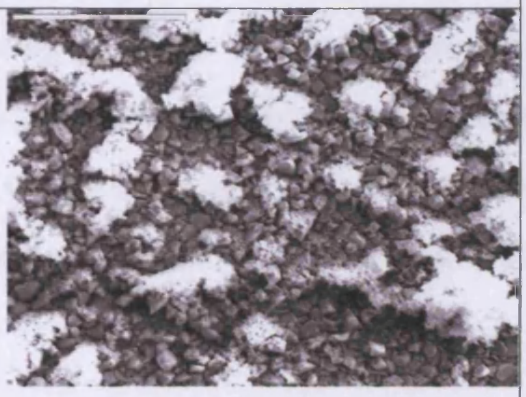


Figure 5.7.Corroded copper treated with re-used solution of 0.25M BTA for 24 hours. There is formation of whitish precipitate on top of the copper oxide crystals.

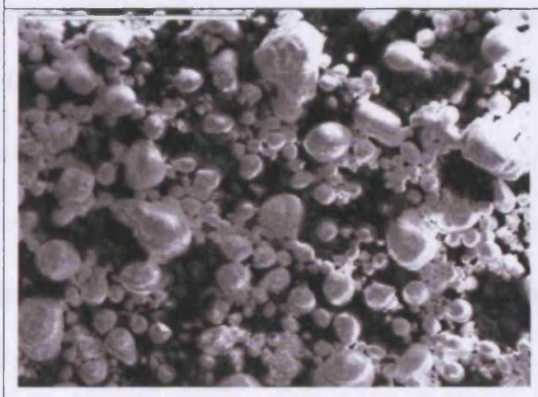


Figure 5.8.Corroded coupons treated with 0.25M for 24 hours after 24-hour exposure to 95±5% RH.

Figure 5.9. Detail of corrosion "lifting" BTA film after 24-hour exposure to 95±5% RH.

5.6.2 SEM-EDS semi-quant linescans

The SEM-EDS semi-quantitative linescans were used as a preliminary analysis of the copper-BTA films, before other methods of analysis were carried out (i.e. FTIR, XPS). In these linescans the distribution of elements across a line on the surface of the coupons were examined. The results that are presented here were used to identify possible patterns that elements, such as C and N representing benzotriazole followed, in relation to the pre-existing elements/compounds of the coupons (copper, chlorine and oxygen representing metallic copper, copper oxides and copper chloride). The linescans of corroded copper showed that chlorine reflects inversely copper. Oxygen on the other hand seems to follow copper. Surface mapping was also considered however the results did not show any significant change over the surface.

5.6.2.1 Comments on SEM linescans

Since nitrogen is bonded to copper it was expected than in the linescans nitrogen would follow the copper pattern. The results showed the opposite. This could indicate that there is an uneven precipitation of the copper-BTA film which might be due to the irregular surface, or maybe the un-reacted BTA precipitant. Although this type of analysis is not sensitive enough to explain the mode of film formation, it was interesting as a 'snap shot' of the surface.

As expected the concentration of the solution affects the thickness of the film as indicated by the semi-quant linescans. Nitrogen and carbon were found at higher percentages than

copper in coupons treated with more concentrated solutions (i.e.0.25M). The solvent affected the distribution of the elements (especially that of carbon) to a smaller degree. The time of immersion affected the thickness of the film consequently, the percentages of carbon and nitrogen were higher after longer periods of immersion. Although the thickness of the film does not necessarily denote effectiveness of a treatment, it was interesting to see how the factors affecting the inhibitive efficiency of a solution alter the appearance of the copper surface on a microscopic level. On the whole nitrogen and carbon inversely follow copper with some exceptions that might be also due to contamination of the samples from the environment (e.g. carbon). These observations were also evident on coupons treated with pre-used BTA solutions.

5.7 Analysis of Cu-BTA film

The experimental results showed that the time of immersion, the concentration of the solution and the solvent affect to a lesser or greater extent the efficiency of BTA. The following analyses of copper treated with different BTA solutions using FTIR and XPS aimed to investigate the chemical nature of the way in which BTA is bonded to copper and how the film formation reflects the efficiency variations encountered.

Previous studies have shown that the polymerisation of the copper-BTA film, the thickness of the film, the degree of BTA adsorption into the copper substrate and subsequently the degree of corrosion prevention BTA provides, depend on many interrelated factors (Cohen *et al*, 1990, Brusic *et al*, 1991). However, most of these studies were performed on either metallic copper, or copper covered with thin air-formed copper oxides.

BTA is known to be bonded to copper through either the nitrogen N3 or N2 of the triazole ring and in case of copper oxide the Cu-BTA bond is also stabilised through a hydrogen bond between N-H or C-H and oxygen anion (Jiang *et al*, 2004:12856).

Most of the studies indicate that the type of oxide present on the copper surface can affect the type of Cu-BTA complex formed, whether this will be two or three dimensional and whether BTA complexes with copper I, copper II or both (Nillson *et al*, 1989: 306-326).

The role of other elements such as chlorides or oxygen present in corroded copper as a part of different corrosion products is yet to be established. Cotton and Scholes (1967: 1-5) suggested that the Cu(II)-BTA complex can include other anions such as chlorides and oxygen. Brostoff (1997: 99-107) studied the way BTA bonds with different copper compounds typically found on corroded copper using FTIR and XPS and confirmed that the presence of copper chloride affects the Cu-BTA complex in terms of homogeneity. The presence of a Cu-II-BTA complex is considered less stable than that of Cu(I)BTA and it appears mainly on areas with copper chloride.

5.7.1 FTIR analysis of BTA

One of the main objectives of this analysis was to identify the way BTA complexes with copper and whether this is affected by the copper substrate and existing copper compounds or the solution and the method it has been applied with. Different studies have shown that there is more than one Cu-BTA complex formed and the substrate dictates which this will be. The stability of these complexes, and consequently the corrosion protection they

provide, varies depending on whether they are cuprous or cupric derivatives. Other elements such as chlorides could be incorporated into the Cu-BTA complex. The presence of oxygen and its role in the film formation is yet to be established. It is understood that the corrosion inhibition mechanism is a very complex process subject to many variables.

Three methods were used to examine the copper-BTA complex using FTIR. In one, solid BTA and copper compounds (minerals) were mixed with KBr to form pellets. In the second, clean and corroded copper coupons treated with different BTA solutions were analysed using reflectance absorption. Finally non-aqueous BTA solutions were analysed. In chapter 4 the FTIR methods and techniques used were discussed in depth. The greater part of the analysis was carried out in the mid infrared region (4000-400 cm^{-1}), with some exceptions (i.e. minerals) that are discussed separately. The interpretation of the results is complicated and in order to draw more conclusive results the FTIR analyses should be compared with other analyses to complete the picture. Therefore the FTIR results are reviewed here primarily but are later coupled with the XPS analysis to draw conclusions about the BTA mode of action and the complexes it forms with copper in each case.

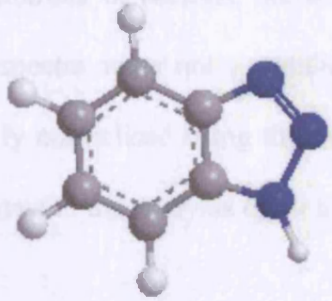


Figure 5.10. BTA molecule showing the benzene ring on the left and the triazole ring on the right.

The assignment of the peaks found in the spectra collected was based on reference BTA spectra analysed and on published literature on the spectral interpretation of copper-BTA. The main peaks identified in aromatic compounds containing benzene rings are, 3100-3000 cm^{-1} where there is C-H stretching, a weak band between 2000-1700 cm^{-1} where there are combination bands, 1620-1400 cm^{-1} ring modes, 1200-1000 cm^{-1} for C-H in-plane bending and 1000-700 cm^{-1} where the C-H out-of-plane bending takes place (Smith, 1998: 51). BTA also has the triazole ring that is of great importance as the bond between copper and BTA happens through the nitrogen of the triazole ring.

The reaction of BTA with copper is evident by the change in N-H stretching bands at 3200-2800 cm^{-1} and 1600-1000 cm^{-1} (Brostoff 1997: 99-108). The differentiation between Cu(I) and Cu(II) complexes is possible as they present some differences in the region 1150-1300 cm^{-1}. In many cases the distinction is not clear as there are peaks corresponding to both copper I and copper II BTA derivatives.

In general, both copper I and copper II complexes with BTA were found. In some cases there is a 2-5 cm^{-1} shift in the peaks from those found in some references that can be subject to a number of reasons, including the alignment and the setting of each instrument used. The spectra were not normalised as is often common (in the case of BTA spectra are usually normalised using the benzene ring at 745 cm^{-1}). Nonetheless, great care was taken to carry out the analysis of all the treated coupons under the same conditions.

Reference spectra of BTA powder mixed with KBr pellets were obtained initially. Since BTA complexes with copper through the nitrogen of the triazole ring, the benzene ring is not affected by the reaction of BTA with copper. The main identification peaks found in BTA were at 741 cm^{-1} which represents the benzene ring, at 1208 cm^{-1} where the stretching of the triazole ring happens, at 1006 cm^{-1} where the N-H in-plane stretching takes place, at 707 cm^{-1} (N-H), at 777 cm^{-1} (C-H), 1384, 1420 and 1459 cm^{-1} (aryl and triazole ring stretching), 1078 and 1622 cm^{-1} (aryl ring mode), 2361, 2709, 2793, 2841, 2909, 2959, 2991 representing the intermolecular stretching of NH···N, 3033 and 3078 (aryl C-H stretching), 3146 (free N-H stretching), 610 (triazo ring torsion) and a wide weak peak at 3247 and 3342 cm^{-1} (N···HOH and NH···OH_2 stretching).

Since the corroded coupons are covered with nantokite (CuCl) and cuprite (Cu_2O) analyses of pure CuCl and Cu_2O mineral powders treated with BTA in ethanol were also carried out. The BTA to mineral powder ratio was 3:1. The powders were weighed and placed in a Petri dish with BTA for an hour, then dried at 105°C for another hour and mixed with KBr to form a pellet. The two spectra were very similar. The peaks of CuCl-BTA in the region 3200- 2700 cm^{-1} are weaker when compared to those of Cu_2O. The main peaks remain the benzene ring at 740 cm^{-1} in case of Cu_2O and 744 cm^{-1} for CuCl. The second strongest peak in both cases was found at 1208 cm^{-1} indicating unreacted BTA. In both spectra there is a weak peak at 1147 cm^{-1} indicative of Cu(I)BTA. In case of Cu_2O a second peak found at 751 cm^{-1} could be another cuprous-BTA derivative. There were peaks present only in Cu_2O-BTA (like 1459, 1308, 1078 and 1047 cm^{-1}) or CuCl (1480, 1792 783, 640 cm^{-1}). In CuCl there is also a weak peak at 1225 cm^{-1} indicating the presence of cupric derivatives.

The peak at 1180 cm^{-1} indicated that there is more than one cupric derivative. This peak has been identified to represent a cupric-chloride-BTA derivative. As a conclusion, the minerals of cuprite and nantokite reacted with BTA to form both cuprous and cupric complexes. In the first case, cuprous-BTA complexes are predominant whilst in case of CuCl cupric complexes are prevailing.

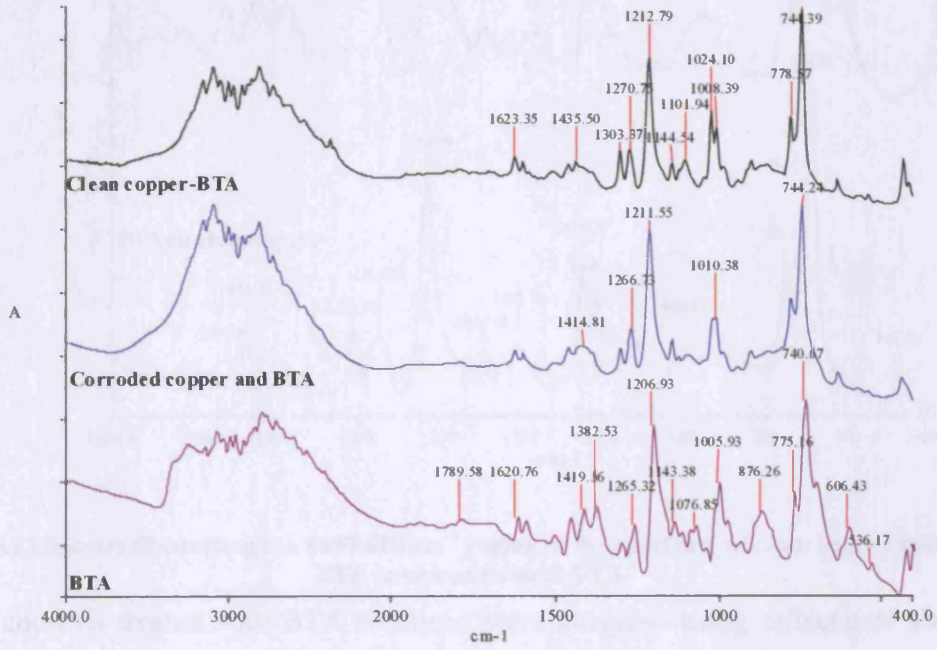


Figure 5.11. FTIR spectra of BTA and BTA on clean and corroded copper showing the shifting of BTA peaks after bonding with copper.

Cu-BTA powder scraped off a corroded copper coupon treated with BTA was also mixed with KBr to form a pellet. The results showed that some of the peaks found in BTA were missing because of the reaction with copper. Figure 5.12 illustrates the two spectra. There region 3200-2700 cm^{-1} (N-H bonds) is drastically reduced in case of Cu-BTA powder showing the bonding of BTA with copper. The complexing of BTA with copper is evident also from the missing N-H peaks such as the 707 cm^{-1} (N-H wagging). The lack of strong peaks in the region 1600-1300 cm^{-1} characteristic of N-H bonds is also indicative of the Cu-

BTA complex. A very strong peak at 1211 cm^{-1} showed there is cupric-BTA complex. The presence of cuprous-BTA cm^{-1} complex is evident by the peak at 1144 cm^{-1}.

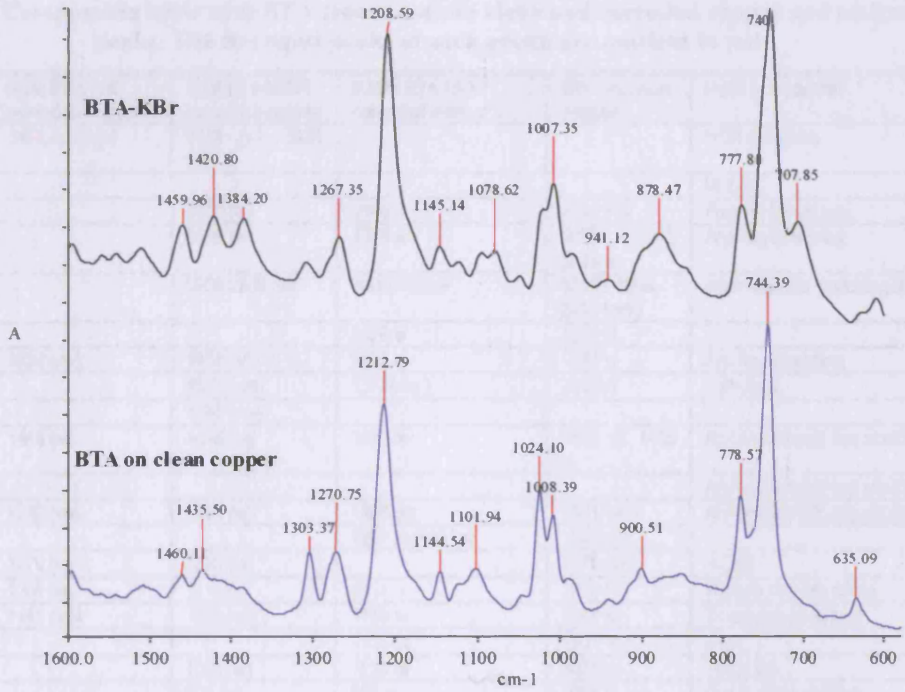


Figure 5.12.Spectra.illustrating the 1600-600 cm^{-1} region of the spectrum of clean copper treated with BTA in comparison to BTA.

Copper coupons treated with BTA solutions were analysed using reflectance absorbance FTIR (see Chapter 4). The samples for the reflectance absorption analysis were prepared following the same procedure described earlier for the accelerated corrosion tests and were cut by hand into 0.5 cm squares to fit into the sample holder. The analysis of the copper-BTA complex on the treated clean and corroded surfaces, especially the corroded coupons was of great significance for this study (Fig 5.11). The samples were kept in an airtight silica gel containing box before the analysis to minimise errors and/or deviations due to uncontrollable environmental factors that could contaminate the surface. The reaction of BTA with copper is evident in the spectra. The main markers are found in changes in the intensity and shifting of the main peaks as well as in the appearance of new peaks. These

changes are representative of the complex formed and whether it is a cuprous of a cupric compound.

Table 5.19. Comparable table with BTA treatments on clean and corroded copper and assignment of peaks. The strongest peaks of each group are marked in red.

BTA powder cm^{-1}	0.1M BTA/H2O corroded copper	0.1M BTA/EtOH corroded copper	0.25M BTA/EtOH corroded copper	BTA on clean copper	Peak assignment
	3446, 3358 (s)	3474 (m), 3424 (w)			HOH stretching
3247, 3342 (w)					NH(...N)
3146 (w)		3150 (w)	3144 w	3150 m?	Free N-H stretching
3033, 3078 (w)		3079 (m)	3078 w	3086 (m?), 3045 w	Aryl ring stretching
3000-2300 (m)		3000-2300 (w)	3000-2415 w	3000-2700w, **2801 (m?)**	intermolecular stretching of NH···N
2361 (m)			2128 w	2362 w	
1622 (m)	1620 (vw)	1618 (w)	1622 m	1623 w	Aryl ring stretching
1540 (vw)		1577 (<m)	1577(<m)	1508 w	ν skeletal
1510 (w)		1491 (<m)			
1459 (m)	1446 (w)	1446 (m)	1450 m	1460 w, 1435 w	Aryl and triazole ring stretching
1420 (m)					Aryl and triazole ring stretching
1384 (m)	1390 (vw)	1394 (w)	1394 ms	1381 vw	Aryl and triazole ring stretching
1307 (w)			1298 m, 1331 w	1303 m?	
1267 (m)	1270 (w)	1273 (m)		1270 m?	δ CH?
1208 (s)	1209 (w)	1214 (s)	1214 s	1212 s	Triazole ring stretching
1145 (w)	1146 (vw)	1150 (m)	1148 m	1144 w	Triazo ring stretching
1094, 1078 (m)			1120 m	1101 w	δ NH
1048 (w)		1028 (w)	1030 m	1024 m	Triazo ipb
1007 (m)		996 (w)	995 w	1008 m	N-H in-plane bending
	832 (w)	834 (w)	848 w	852 w	γ NH (...N)
777 (m)	778 (w)	789 (m)	788 ms	778 m	Benzene and triazole in-plane bending
741 (vs)	745 (m)	745 (s)	750 vs	744 vs	CH opb-Benzene ring
707 (m)			720 w		N-H
	622 (vs)	624 (m)	639 m	635 w	Cuprite
610					Triazo ring torsion
		433 (m)	439, 428 m	427 m, 411w	

The peak identification was based on published literature: Brostoff (1997:101), Nilsson *et al* (1989:306-326) and Bigotto *et al* (1996: 511-522).
s: strong, m: medium, w: weak, v: very, opb: out of plane bending, ipb: in-plane bending.

The main peaks of the more significant treatments examined are listed in table 5.19. In general a shift (slight increase in cm^{-1}) in the BTA peaks is observed because of its reaction with copper.

Clean copper treated with BTA solutions presented similar spectra. Slight changes occurred in the intensity of the peaks, probably due to the thickness of the complex. It is known that a copper oxide film is formed immediately after cleaning of the copper surface. Therefore,

although the copper coupons were mechanically cleaned to remove any oxides present before the treatment, it was not possible to achieve a completely oxide free surface. As a result, BTA formed a complex with the thin copper oxide layer of the surface. Clean copper treated with BTA in ethanol also presented a mixture of cuprous and cupric-BTA derivatives. A lot of N-H bonds are missing from the spectrum indicating the reaction of BTA with copper. The very sharp peak at 744 cm^{-1} is a cuprous-BTA derivative also evident from the 1144 cm^{-1} peak. However, it appears that the cupric-BTA complex is the predominant one seen from the sharp peak at 1212, 1024 and 1271 cm^{-1}.

5.7.1.1 BTA 0.1M in deionised H_2O

The spectrum of 0.1M BTA in water is very interesting, especially when compared to the ones dissolved in ethanol. The main peak found is at 622 cm^{-1} which could be the peak of cuprite (Mendoza *et al,* 2004: 1189-1200). A further two strong peaks are found at 3358 and 3446 cm^{-1} and are representative of HOH stretching/adsorbed water and then 745 cm^{-1} the benzene ring. The other peaks (990, 1147 cm^{-1}) indicate that there is a cuprous-BTA complex formed on the surface. Weak peaks at 681, 1024 and 1395 cm^{-1} signify the presence of Cu(II)BTA complex. No significant changes were observed between copper treated with the same solution for longer except that there was mainly Cu(II) present after 24 hours of immersion. The intensity of the peaks was also higher indicating probably a thicker Cu-BTA film.

5.7.1.2 BTA in ethanol

Coupons treated with BTA solutions of different concentrations (0.25M and 0.1M) were studied. At first glance, the differences found in the spectra were those related to the intensity of the peaks which varied in each case. Copper treated with 0.25M in ethanol also presented a mixture of cuprous and cupric BTA derivatives. However, from the spectra it appeared that Cu(II)BTA complexes were predominant. The following peaks were observed: 750 cm^{-1} (a shift of the 745 cm^{-1}peak of benzene ring), a very strong sharp peak at 1214 cm^{-1} indicating clearly the presence of Cu(II)-BTA complex and also 1394, 1273, 1030, 1120, 1621, 1577, 639 and 563 cm^{-1}. Cu(I)BTA peaks were also found such as 1148, 1597, 1450, 1120 and 1597 cm^{-1}. Peaks such as 788 and 1492 cm^{-1} are attributed to both cuprous and cupric derivatives. Longer periods of immersion resulted in a slight increase of Cu(II)-BTA peak intensities (Fig. 5.12).

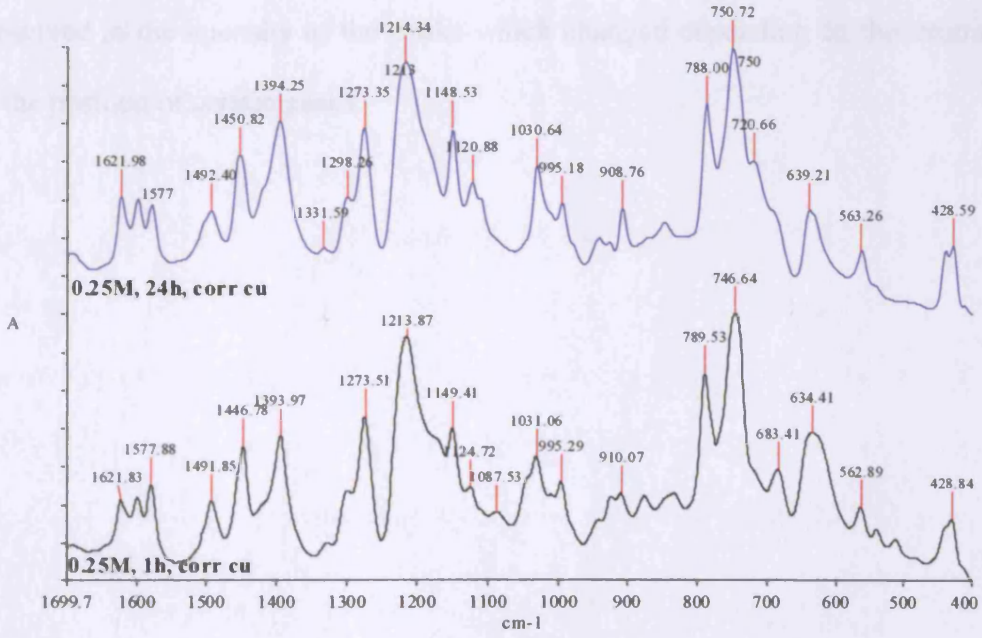


Figure 5.13. Absorption reflectance of corroded copper coupon treated with 0.25M BTA after 1 and 24 hours of immersion

A lower concentration of BTA in ethanol (0.1M) showed clearly that there were also both cuprous and cupric complexes with the latter type prevailing. The main peaks are shown in table 5.19. Of great interest is that there was a strong peak at 1171 cm^{-1} which may be a Cu(II)-Cl-BTA complex which was not found in the case of 0.25M. Another interesting peak found was that of cuprite at 626 cm^{-1}. The same peak, although with a small shift, was found in the same concentration solution dissolved in deionised water.

From these results it is clear that both concentration and solvent affect the formation of the Cu-BTA complex formed on the corroded copper surface. Interestingly, chlorides seem to have been incorporated in the complex in the case of 0.1M in ethanol. A very weak peak at 1180 cm^{-1} in coupons might indicate this. It is obvious that although some of the main peaks remain the same there were differences between BTA dissolved in ethanol and water, illustrating that the solvent affects the complexing of BTA with copper. These differences were observed in the intensity of the peaks which changed depending on the treatment as well as the position of certain peaks.

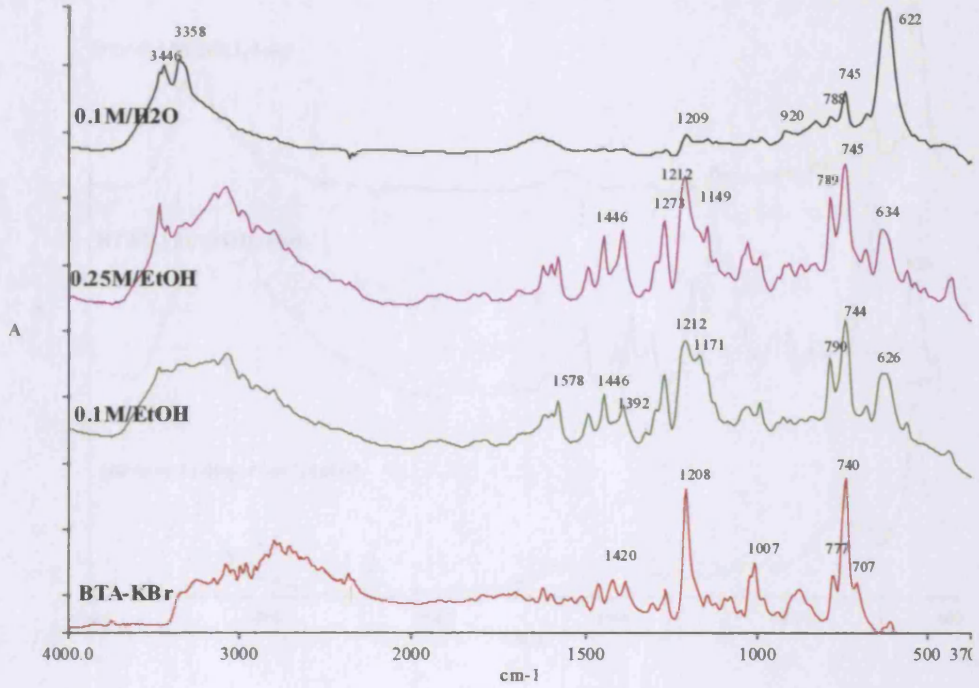


Figure 5.14. Comparison between different BTA treatments. The effect of the solvent and the concentration

Figure 5.13 shows the spectra of corroded copper treated with 0.25 and 0.1M BTA in ethanol and 0.1M in deionised water. Of great interest was the comparison between 0.1M in deionised water and ethanol. In the first case, the main peak was that of cuprite at 622 cm^{-1} which is most probably related to the cuprous-BTA complex whilst in the second case, the strongest peak was that of 745 (C-H bond). The cuprite peak existed even in case of a coupon treated with 0.1M in ethanol. This peak might mean that either that there was interaction of BTA with cuprous oxide to form Cu(I)-BTA complex on the surface, or less possibly that during the treatment there was further oxidation of the surface to form new cuprous oxide (Fig. 5.14)..

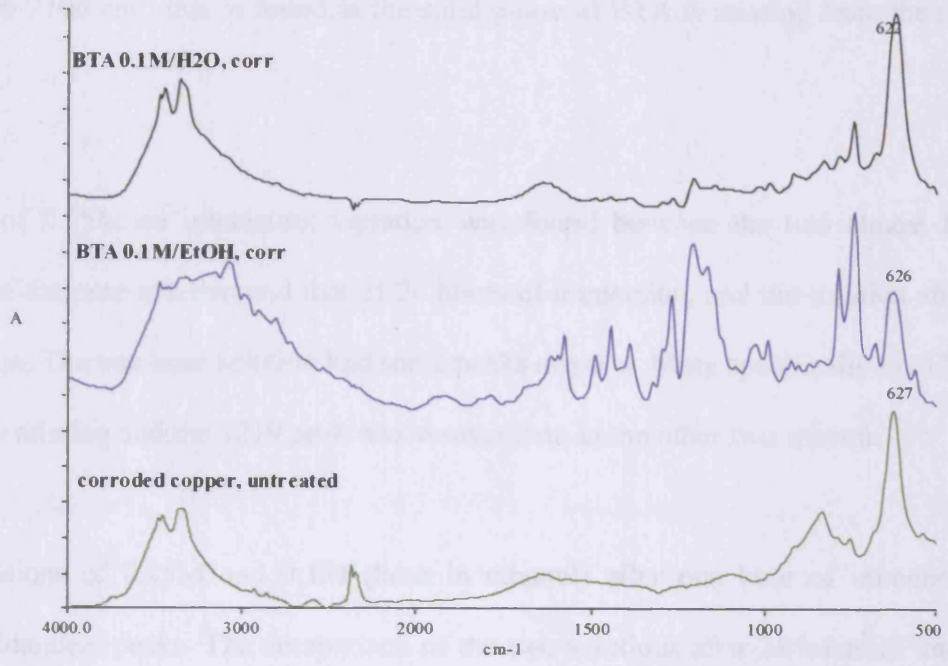


Figure 5.15. Spectra of corroded copper treated with 0.1M BTA in deionised water and ethanol. The peak of cuprite at 622 cm^{-1} is the strongest in aqueous treatment.

5.7.1.3 Analysis of non-aqueous BTA solutions

Apart from the reflectance absorption analysis of copper treated with BTA, non-aqueous BTA solutions were also analysed. One of the objectives of this analysis was to examine whether copper ions dissolved in solution were complexing with BTA to form complexes that would later precipitate as a protective film on the metal surface. This could give an indication about the actual BTA mechanism on corroded copper. Solutions of BTA dissolved in ethanol at 0.1M and 0.25M were analysed. Following this the solutions were also analysed after 1h and 24 hours of copper immersion. The ethanol spectrum (solvent) had to be subtracted by the spectra of the solutions to examine the solute (BTA). The intensity of 0.25M solution was greater than that of 0.1M. The broad band of peaks in the

area 3400-2100 cm^{-1} that is found in the solid phase of BTA is missing from the solutions (BTA^-).

In case of 0.25M an interesting variation was found between the two almost identical spectra of the pure solution and that of 24 hours of immersion, and the solution after 1h of immersion. The one hour solution had some peaks missing. More specifically the 1712 cm^{-1} peak was missing and the 1219 peak was weaker than in the other two spectra.

The solutions of 0.25M and 0.1M (both in ethanol) after one hour of immersion also showed identical peaks. The comparison of the two solutions after 24 hours of immersion showed a difference in that the peaks 1712, 1220 and 1360 cm^{-1} were found only in the solution of 0.25M.

The solutions that were used more than once were also analysed (see experiments 5-8). No great differences were found in the spectra of 0.25M/EtOH, the spectra were almost identical. There were some differences in one of the re-used solutions, but not significant ones. The strongest peak was found to be 1219 cm^{-1} showing that a Cu(II)BTA derivative is present in the solution in agreement with the cupric derivatives found on the copper coupons treated with BTA. This indicates that they are not only the result of oxidation of the Cu(I)BTA complex, therefore they are not a by-product.

The spectra of the re-used BTA solutions analysed were found to be identical. The strongest peaks found were those of 1220 and 1360 cm^{-1}. In conclusion, both Cu(I) and

Cu(II) BTA complexes exist in solution and the film formed on the surface could be a result of a dissolution-precipitation mechanism.

Copper corrosion products taken from the corroded coupons and pure copper compounds (cuprite, nantokite) were also analysed. The main identification peaks of minerals are found in the far infrared region (<700 cm^{-1}) whilst the organic compounds (i.e. inhibitors) are traced in the mid infrared region (700-4000 cm^{-1}) which required a change of the detector of the spectrometer. The analysis was carried out by mixing the compounds with KBr to form a pellet. The comparison between the pure cuprite and cuprous chloride (nantokite) with powder of corrosion products from the corroded coupons, confirmed the XRD results regarding their presence in the coupons (nantokite peak at 172 cm^{-1}). The spectra and peak tables are given in Appendix 5.

BTA powder was also analysed in the far infrared region. The results showed some peaks at 427, 409 cm^{-1} (torsion and in-plane bending), 287 cm^{-1} (torsion), 274 cm^{-1} and a wide band of peaks between 220-48 cm^{-1} representing the crystal lattice.

FTIR could also be used to calculate the thickness and orientation of the film. Nillson *et al* (1989: 306-326) using FT-IRAS did a "coarse" calculation of the thickness of a BTA film on cuprous oxide films of different thicknesses and found that the thickness of the Cu-BTA film varies accordingly. On a thicker oxide layer, the BTA film is thicker than on a thin oxide substrate. However, the results of the analysis in this chapter showed that there was more than one Cu-BTA complex formed in most of the samples analysed. The films could

be multilayered cuprous and cupric-BTA polymeric chains and maybe not even uniform throughout the surface, so calculations of the thickness could not be of use.

One of the limitations of the reflectance method used is that visual observation of the area analysed is not possible. The treated coupons were not always covered with uniform Cu-BTA films as can be seen in the SEM images. The analysis of more than one selected area of the same copper coupon could have been possible using a FTIR microscope however this was unfortunately not feasible as the corroded samples were not transmitting enough signal due to noise with the available microscope. The results, although representative of the surface films analysed, cannot be absolute for all corroded copper surfaces treated with BTA solutions.

5.7.2 XPS

The aim of the XPS analysis was to investigate whether the Cu-BTA complex formed was dependent on the metal surface and the corrosion products present and to what extent. Another question that arose from the accelerated corrosion testing was how different BTA solutions bonded to the copper and how the Cu-BTA complex and the film formation was affected by selected factors tested. To answer these questions numerous samples of copper coupons treated with different BTA solutions were analysed. The results were fairly consistent in terms of reproducibility.

The way other elements present in the corrosion products (in this case, chlorides and oxygen) were incorporated, if at all, in the film formed was of great interest. The FTIR results showed that in many cases chlorides are part of a cupric-chloride-BTA complex, the exact composition and structure of which is not known.

Clean and artificially corroded coupons treated with different BTA solutions were analysed. The main elements investigated were, copper, oxygen, chloride, carbon and nitrogen. The first three elements represent the copper (copper coupons of metallic copper with some air formed Cu_2O and corroded coupons covered with Cu_2O and CuCl) whilst carbon and nitrogen are the main constituents of BTA. Hydrogen is not detectable with XPS. Untreated clean and corroded copper coupons and BTA on glass were analysed at first as a reference and the analysis continued with clean and corroded coupons treated with different BTA solutions. This was to examine how factors such as the concentration of the solution, the length of time of immersion and the solvent used might affect film formation and thus the efficiency of BTA.

Of great interest were the differences in film formation between clean and corroded copper. The binding energies of the selected elements are presented along with possible bonds or compounds they represent. Finally the atomic percent concentrations of the elements analysed and their ratios are also presented.

5.7.2.1 Clean and corroded copper

The peaks found on clean copper were those of metallic copper and air formed copper oxides Cu_2O and CuO, and some carbon detected (due to contamination). The presence of the copper oxides was predictable as metallic copper is very reactive and oxides are formed on the surface quite rapidly. The distinction between cuprous and cupric oxides using XPS analysis is possible because cupric oxide has strong satellite peaks that cuprous oxide lacks (Millet *et al*, 1995: 1907). The ratio Cu^{+}/Cu^{++} was found to be 10.

Different studies agree with the results found. Chawla *et al* (1992: 1617-1631) found an air formed cupric oxide and bound hydroxyl and water absorbed on the copper oxide after its formation. Others also confirm the presence of cupric oxide on top of cuprous oxide.

The artificially corroded copper coupons included copper chloride (CuCl, nantokite) and copper(I) oxide (CuO_2, cuprite). The analysis showed, unsurprisingly, Cu_2O, some CuO and CuCl. Hydroxyl and water clusters (OH/H_2O) were also found, possibly due to water absorption from the environment (table 5.19). The samples were kept in a desiccated environment in a sealed box, however during sample preparation they were exposed to ambient environmental conditions. Some carbon was also found due to contamination from the environment. The presence of some CuO was expected as cuprite is not thermodynamically stable in air and a thin layer of CuO forms at the outermost level (Xu *et al*, 1993: 995).

Table 5.20. Main copper and oxygen XPS binding energies (BE) of clean and corroded copper coupons used as reference.

Sample	Element	Binding energy (eV)	Compound
Corroded copper	Cu2p3/2	932.1, 951.7	Cu_2O, CuO, $Cu(OH)_2$?
Clean copper		932, 934, 951	Cu_2O, CuO
Corroded copper	O1s	529, 530	
Clean copper		531	

The BTA solution was applied by brush on a glass slide and was allowed to air dry before the analysis. The peaks found were those of carbon (284.5eV), nitrogen (a wide and relatively weak peak at 400.7eV with shoulder peaks at 399eV and 402eV), a strong although wide oxygen peak (532.5eV) and silicon (glass slide was made of Si_2O, the silicon peaks were found at 102 and 152.5eV). The oxygen which was the strongest peak (7000 counts/sec) comes mainly from the glass substrate (as it is also obvious from the ratio between Si and O) some due to atmospheric contamination and some remaining from the aqueous BTA solution used.

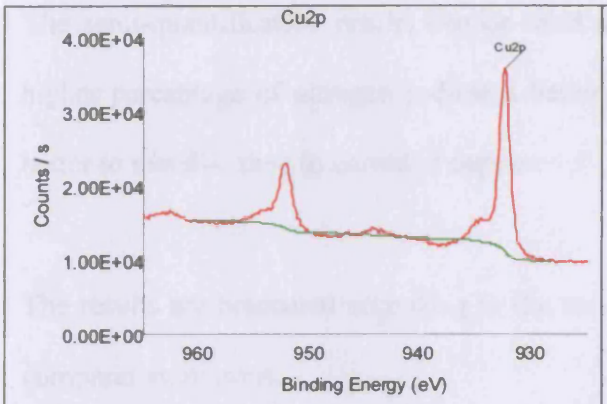


Fig. a. Clean copper coupon Cu2p

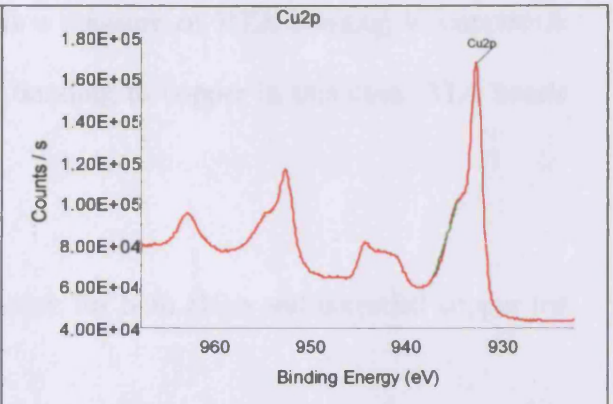


Fig. b. Corroded copper coupon Cu 2p

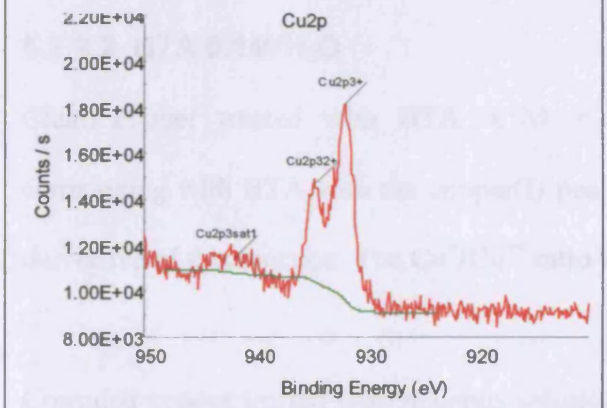


Fig. c. Clean copper treated with 0.1M BTA/H_2O (CuI and some CuII)

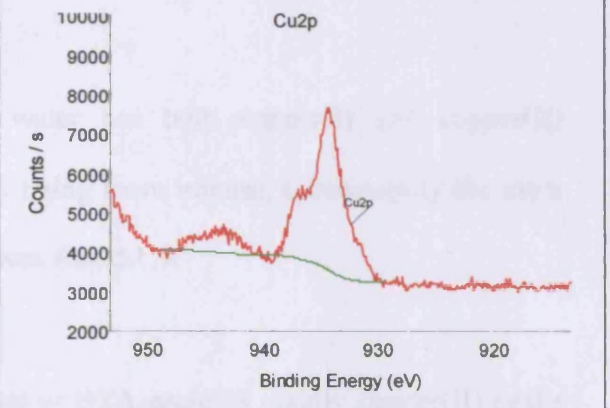


Fig. d. BTA 0.1M/H_2O, Cu2p (CuII and some CuI)

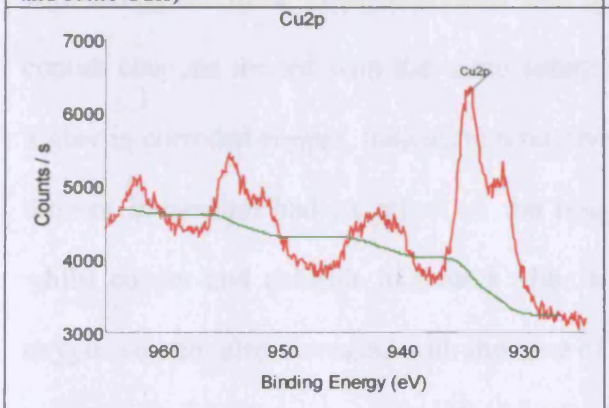


Fig. e. Clean copper treated with 0.25M BTA/EtOH, 1h, (CuII and some CuI)

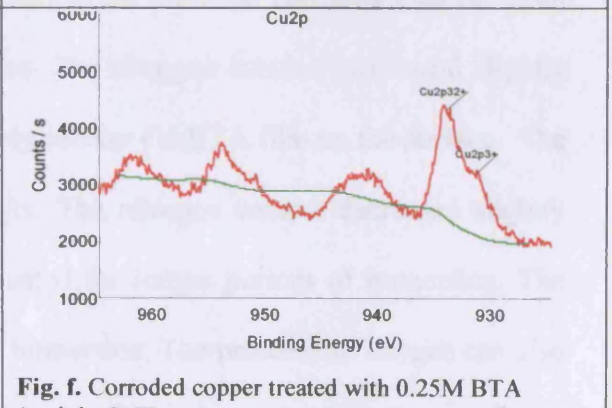


Fig. f. Corroded copper treated with 0.25M BTA (mainly CuII)

Figure 5.16. (a-f). Comparison of Cu2p XPS spectra of clean and corroded copper and different BTA treatments.

The semi-quantification results can be used as a measure of BTA bonding to copper. A higher percentage of nitrogen indicates better bonding to copper in this case, BTA bonds better to metallic than to corroded copper.

The results are presented according to the solution for both clean and corroded copper for comparative reasons.

5.7.2.2 BTA 0.1M/H_2O

Clean copper treated with BTA 0.1M in water has both copper(I) and copper(II) complexing with BTA with the copper(I) peak being more intense, subsequently the main derivative of this reaction. The Cu^{+}/Cu^{++} ratio was found 1.9.

Corroded copper treated with aqueous solutions of BTA presents mainly copper(II) peaks with strong satellites. Oxygen content was found to be lower on corroded than on clean copper coupons treated with the same solutions. The nitrogen content was found slightly higher in corroded copper, indicating a relatively thicker Cu-BTA film on the surface. The time of immersion had an effect on the results. The nitrogen content decreased slightly whilst copper and chloride increased when treated for longer periods of immersion. The oxygen content also increased with the time of immersion. The presence of oxygen can also be indicative of water adsorption. The elemental ratios found lower for BTA:Cu and higher for O:Cu and Cl:Cu.

These results could explain the failure observed in the accelerated corrosion tests, where longer immersion of coupons in aqueous BTA solution results in accelerated corrosion rather than inhibition. In general, higher oxygen content was found in coupons treated with aqueous BTA solutions.

Table 5.21. Binding energies (eV) of main copper and BTA elements used.

Sample	Cu2p	O1s	Cl	C1s	N1s	Possible compounds
Clean copper	932.18, 951.78	529.9-530.8 and 530			n/a	Cu2O, CuO, possibly Cu(OH)2
Corroded copper	932.1(CuCl), 951.78	531 and 535.587	Very low 194.6, 196.3		n/a	Cu2O, CuO, 535 of O1s, clusters of OH/H2O?
BTA (on glass)		532.5 (very strong peak)		284.5	400.7 (and 399.3 and 401.9)	O due to SiO2
BTA 0.1M/H2O, clean copper	932.2, 934.9, sat 943.1	532.1 (very low)		284.5	399.8	
BTA 0.1M/H2O, corroded copper	934.3, 936.5, 953, sat 943.3	Low (532)	Very low 197, 198.9 (199.5)	284.5	400.6 (sat 407.5)	
BTA 0.1M/EtOH, corroded copper	935, 954.7, 962.8, sat 942.5 and very low 932	Very low at 531.9	197.7, 199.6 (or 198.9)	284.55	399.9 (400.45)	
BTA 0.1M/EtOH, corroded copper FRESH a	934.8 (low 931.7), 954.3, 962.4, 951.7, sat 942.8	Low (531.8)	197.7, 199.4	284.4 (stronger)	399.8	
BTA 0.1M/ EtOH, corroded copper b	934.9 (low 932), 954.4, 962.6, 951.8, sat 942	Low (531.8)	197.9, 199.4	284.5	399.8	
BTA 0.1M, corroded copper, 1h	935.3 (Cu(OH)2), 943.9 (C-N)	531	197.8, 199.3	284.4	400 (N2H4m N2, NH3, NH3?)	
BTA 0.25M 1h clean copper	934 (CuII-N) 931.3, 951, small peak and 960	531.5 (v low)		284.5	399.6 (C-N, or N-O?)	Cu2O, CuO, Cu-N
BTA 0.25M 24h clean copper	934.7 (CuII-N, Cu(OH)2, 931.6, 954.3, 951, 961, 941	532		284.5	399.6	
BTA 0.25M, 1 h	935, 933, 956.3, 953, 943.5 (C-N sat), 964	No oxygen	Low double peak 197, 199 (CuCl2)	284.5	399.8 (C=N), (sat at 407?)	
BTA 0.25M, 24 h	934.1 (Cu-N), (931?), 955, 952, 964, 943 (Cu-N sat)	No oxygen	Very low 197, 199.7	284.7	399.7 and 400.4 (sat at 407?)	
BTA 0.25M, corroded, after 24h at 95%RH, 25°C, area 1	934, 953, strong satellite peaks	No oxygen	Low, wide peak at 198	Wide peak 284.5	399.4 and sat	
BTA 0.25M, corroded, after 24h at 95%RH, 25°C, area 2	930.5 and 950.5 with strong satellites at 937.5 and 957	Very low 529.4	Wide peak at 200	Very low 284.7 and sat at 268.7	Double peak 392 and 397.7	Sample was charging

The analysis of corroded copper treated with 0.1M in ethanol showed that BTA in this concentration is mainly bonded to copper II. The Cu^{+}/Cu^{++} ratio was found to be 0.2. The atomic concentration percentage of oxygen was very low (<1at%). An interesting result was related to the ratios between the elements that were found to be similar to those of the coupons treated with equimolar aqueous solution for an hour although the percentages of the elements varied. However, it is important to note than although the ratios were similar, the film formed was different, with aqueous BTA solutions react with copper(I) or copper(II) depending on the period the coupon stayed immersed in the solution, whilst in the latter case, the time of immersion did not influence BTA bonded mainly to copper(II).

5.7.2.3 BTA 0.25M

On clean copper, the Cu-BTA complex formed is a mixture of copper(II) and copper(I) - BTA derivatives with the former predominating. Time of immersion affects only slightly the film formation. BTA is mainly bonded to copper(II) when applied on corroded copper. Oxygen content is higher on clean copper (6at%) than on corroded copper treated with BTA for both 1 and 24 hours of immersion. The oxygen peak is sharp for clean copper whilst is practically non-existing on corroded copper treated with using this concentration.

Another interesting element is nitrogen. On clean copper, there is a sharp nitrogen peak whilst on corroded copper there are two peaks (at 399.7eV and 400.4eV) and a ghost satellite peak at 407eV.

Corroded copper treated with solution of 0.25M in ethanol showed that BTA is bonded to both copper(I) and copper(II) with the latter being predominant. The Cu^{+}/Cu^{++} ratio was found to be 9 for clean copper and 0.6 for corroded copper.

5.7.2.4 Elemental quantification

The analysis of BTA on glass slide showed high carbon and oxygen percentages (oxygen quantity explained because of SiO_2 of the glass slide). Nitrogen was found to be approximately 11at%. Copper treated with BTA solutions showed higher percentages of nitrogen (over 20at%) because of the bonding of BTA to copper. The analysis carried out on copper treated with different BTA solutions present similar nitrogen content with minor deviations. More specifically, the nitrogen concentration seems to decrease slightly for treatments involving longer times of immersion indicating a probable thicker film formation on the surface. Interestingly, the concentration of chlorine increases with time of immersion.

Table 5.22. XPS At% ratios of elements analysed on corroded and clean copper coupons treated with different BTA solutions. * N/3 represents BTA bonding to Cu therefore this ratio is given separately.

BTA	0.1/H_2O, corr	0.1/H_2O 24h, corr	0.1/EtOH 1h,fresh, corr,	0.1/EtOH 1h-old, corr,	0.25M, 1h corr,	0.25M, 24h, corr	0.25M, 24h after exposure to 95% RH	0.1M/ EtOH, clean	0.25M, clean	0.1M/H_2O, clean Cu
N:Cu	3.5	1.9	3.5	3.5	9.5	4.4	2.6	6.8	10.0	2.8
(N/3): Cu*	1.2	0.6	1.2	1.2	3.2	1.5	0.9	2.3	3.3	0.9
O:Cu	0.2	0.6	0.2	0.1	0.0	0.1	0.6	2.1	2.5	0.5
Cl:Cu	0.3	0.9	0.6	0.6	1.2	0.6	0.7	0.0	0.0	0.2

The ratios between selected elements (Cu, O and Cl for copper, N for BTA, carbon cannot be used because some of the content is due to contamination of the surface) showed that as a general rule there is more oxygen present when BTA complexes with clean copper (table

5.21). The lowest oxygen content was found on corroded copper treated with 0.25M in ethanol. Although as has been mentioned earlier, the content of nitrogen is found to be at the same levels in most treatments, nitrogen to copper ratio varies because the content of copper changes markedly depending on the treatment. In general, the concentration of the solution and the solvent used affect the elemental ratios. A higher concentration results in higher nitrogen to copper ratios and lower oxygen to copper ratio. The chlorine to copper ratio seems to be at the same level, with few exceptions. Interestingly, the time of immersion affected both the oxygen to copper and nitrogen to copper ratios. Longer periods of immersion seem to result in lower nitrogen to copper ratio. This is found of particular interest, especially when examined with the accelerated corrosion testing where the time of immersion had a negative effect on the efficiency. Although in theory longer immersion in the solution should result in increased effectiveness, the ratios show that there is less nitrogen bonded to copper.

Corroded copper treated with solution of 0.25M in ethanol for 24 hours was analysed before and after exposure to high RH (95±5%). The results showed that after the exposure, copper, oxygen and chloride contents are increased, carbon levels decrease and nitrogen remains at the same levels. It seems that the BTA formed a quite thick layer of Cu-BTA complex which was, however, affected by the humidity. The oxygen levels can be a direct effect of the humidity on the metal and/or the copper-inhibitor film formed on surface. What was noteworthy was that the nitrogen to copper ratio dropped by almost 50%, whilst the oxygen to copper ratio increased. The Cu^{+}/Cu^{++} ratio was found to be 0.5. Finally, there

was no difference in the elemental ratios between coupons freshly treated coupons and coupons that remained for 2 weeks in a silica-gel desiccated box.

5.7.2.5 Conclusion on XPS analysis

The copper-BTA film formed on copper is a mixture of Cu(I)-BTA and Cu(II)-BTA, the percentages of which differ depending on the copper surface, the concentration of the mixture and the time of immersion. The thickness of the film varies accordingly. Clean copper shows higher percentages of nitrogen and has mainly Cu(I)-BTA and little oxygen. The Cu-BTA complex on corroded copper does not incorporate oxygen it does however incorporate chlorides. BTA 0.25M immersed for an hour was the treatment that was found to be the most effective in accelerated corrosion testing, it has higher nitrogen than those treated with the solution for 24 hours.

5.7.2.6 Oxidation/reduction reactions during XPS analysis

It has been reported that copper could change valence during XPS analysis (cupric derivatives to be reduced to cuprous during the analysis) it was found therefore necessary to run several experiments analysing the same sample more than once to check whether it happens or not. If changes were to occur during the course of the actual analysis, some of these changes could be detectable.

Analysis of samples allowed qualitative evaluation of these changes. Corroded copper coupons were analysed a few hours after their treatment with BTA 0.1M/EtOH. The same coupons were analysed twice whilst in the chamber to monitor possible alterations of the

Cu-BTA compounds. The results were also compared with those of Cu-BTA on a coupon that was treated two weeks before the actual analysis took place.

The results showed that there are no significant differences therefore there was no oxidation or reduction of copper species occurring during analysis. The main reason was that the analysis was carried out using a monochromatic source not a twin source that could cause reduction.

5.7.2.7 Angle-resolved measurements

Angle resolved measurements took place on a sample of corroded copper treated with benzotriazole. By changing the direction of the sample, the source emission changes, allowing the depth profiling of the sample. The angle-resolved measurements took place at 0° and 85° degrees.

Table 5.23. Semi-quantitative data of angle resolved measurements of BTA.

AR-BTA	0°	85°
Cu2p	13.8	8.4
C1s	52.0	62.8
Cl2p	3.4	2.1
N1s	28.6	21.0
O1s	2.1	5.8
Cu^{+}/Cu^{++}	7	2.4

The change of angle helped to examine the copper-BTA film formed at different depths, where the 0° refers to the inner layers and the analysis at 85° represents the outer layers. The results showed some differences at the different angles. More specifically, there was a small difference between the Cu2p. There was obviously a lot more copper at 0° with mainly copper(I) and some copper(II). Also at 85° there was more copper(II) than at 0°. The Cu^{+}/Cu^{++} ratio was found to be 7 at 0° and 2.4 at 85°. Nitrogen and carbon indicate the

presence of benzotriazole and whilst carbon content was higher at 85°, nitrogen was lower. In this case, it was evident from the analysis that benzotriazole is adsorbed into the copper substrate (table 5.22). The oxygen percentage (at%) was lower at 0° than 85°. In latter, the peak was very wide at 531eV, 532eV and 539eV indicating the presence of H_2O/OH^- clusters. Fewer chlorides were found on the outer layers (85°).

Even though the experimental conditions were totally different and comparisons are not always possible the results are in agreement with Millet *et al* (1995: 1903-1918) who found copper(II) mainly located at the outer layers and copper I at the inner layers.

5.7.2.8 Comparison of samples before and after exposure to high RH

One of the outcomes of the accelerated corrosion tests was that the efficiency of BTA drops after exposure to high RH. Since 3% (0.25M) in ethanol is the concentration mainly used by conservators, it was decided to analyse the sample before and after the exposure to 95%RH, 25°C. The sample was analysed in two different areas. The first area was dark green and second area was covered with lighter green sediment. Unfortunately, during analysis it was noted that the second area was subject to charging and therefore the results might not be representative. Still from the results it is clear that there is less carbon and nitrogen (representing BTA) after 24 hours in the humidity chamber. Area 1 showed mostly copper(II) and compared to the sample before the exposure, less copper(I). Area 2, showed copper(I) with strong satellites of copper(II). This could be due to a copper(I) compound found there, or an error because of the sample charging. In all cases there was no or very little oxygen. The peaks of the samples after the exposure were a lot less sharp and in case

of nitrogen in area 2 there was a double peak. It is evident that the copper-BTA complex undergoes changes, with further oxidation of copper I to copper II being the more obvious. The quantitative changes found on both nitrogen and carbon, were also important as an explanation for the decreased efficiency of the treatment.

The XPS results are in agreement with those found during FTIR analysis. Corroded copper treated with BTA is covered with a mixture of cuprous-BTA and cupric-BTA derivatives, the ratio of which is dependent on the substrate, the concentration of the BTA solution, the solvent and the time of immersion. Chlorides and oxygen are also incorporated in the copper-BTA complexes the stoichiometric ratio and the structure of the which needs further investigation.

5.8 Discussion

BTA in solution exists in two forms, BTAH and BTA^- with the latter more easily bonded to copper to form an insoluble Cu-BTA polymeric film. The addition of BTA in water decreases the pH and increases the conductivity, both factors normally leading to increased corrosion if it weren't for the inhibitive action of BTA. The concentration of BTA^- depends on the pH of the solution; in alkaline solutions the ionization of BTA increases, whilst in acidic conditions the ionization decreases. Fox *et al* (1979: 457-467) suggested that in slightly acidic pH values, there is adequate BTA^- to react with Cu^{+1} but not enough to react with all the Cu^{2+}.

The BTA pH was found to be slightly acidic ($\approx$ 5.5-5.8) and after immersion of corroded copper coupons it dropped into more acidic values (4.2 after one hour of immersion and 3.6

after twenty four hours). The amount of BTA^- in the solution is crucial for complexing with copper.

BTA is chemisorbed into the copper surface. However, the thickness of the Cu-BTA film implies that more than chemisorption takes place on the copper surface. In theory, the effectiveness of BTA increases with concentration and longer periods of time of immersion. The properties and stability of the copper-BTA derivatives is of great significance for the protection of copper. The corrosion of copper archaeological objects is the end result of long and largely unknown reactions taking place over a number of years. The chemistry and composition of the corrosion products is not always known or explicable therefore uncontrollable. Corrosion inhibition of copper with BTA can be more successful by eliminating known factors such as the results of this chapter. Different polymeric structures have been suggested in the literature for the Cu-BTA complex, the formation of which seems to vary depending on the copper substrate (copper, copper oxide, copper chloride, malachite, etc.) and also in the presence of aggressive ions such as chlorides. The experimental part of this chapter provided data not only about the way the Cu-BTA complex is formed on different copper surfaces but also about how other factors related to the application of BTA affect its structure, consequently the efficiency of the treatment.

From the results it is evident that the copper-BTA complex formed is dependent on the type of copper corrosion product (oxides and chlorides) present on the surface. The accelerated corrosion tests were necessary before the FTIR and XPS analyses were completed. Complicated analytical results and theoretical models can be of no real use without an

established relationship to the effectiveness of a treatment. Their combination can lead to a rational conclusion about the BTA mode of action on corroded copper. In this study the objective was not only to examine how the Cu-BTA complex is formed on different copper substrates but also how this affects the effectiveness of the treatment.

The time of immersion plays a very significant role in the effectiveness of a treatment. According to Nilsson *et al* (1989) prolonged immersion of copper into the BTA solution can cause oxidation of cuprous-BTA into cupric-BTA complex.

The main complex reported in the literature is that of Cu(I)-BTA. However in most cases examined in this chapter it was found that there was a mixture of copper I and copper II BTA complexes. An explanation for this could be that copper I could have been oxidised to copper II. Another is that although in solution a Cu(I)-BTA complex is formed, during drying Cu(I) oxidised to Cu(II). Interestingly, a small quantity of Cu(II) on copper surfaces treated with BTA seems to be little affected by the time of immersion in BTA solutions (Chadwick and Hashemi, 1978: 39-51).

Roberts (1974) also reported that shorter periods of immersion of copper in aqueous solutions of BTA resulted in the formation of Cu(I)-BTA complex, which however was further oxidised to Cu(II)-BTA when the immersion period was extended It is interesting that in the aforementioned paper, even a 3-minute immersion results in Cu-BTA complex on the copper substrate. Copper II-BTA complexes have been reported to be less stable therefore less protective than copper I (Roberts, 1974).

Corroded copper coupons treated with aqueous solutions of 0.1M BTA for 1 hour gave results that, although lower than those of 0.25M and 0.1M BTA in ethanol were satisfactory. The most important factor in the aqueous BTA solution was the time of immersion. The optimum period of immersion is yet to be established.

More experiments are needed to define the length of time of immersion that will give optimum BTA efficiency. In this case, it was very clear that although the aqueous solution would inhibit corrosion when the coupon is immersed for an hour, it would promote corrosion when immersed for twenty four hours.

The use of a lower BTA concentration has the advantage that is more cost effective; the solution can be changed regularly instead of being used over and over again and there is less BTA to dispose into the environment. The toxicity of BTA is debatable and articles, such as Oddy (1972) have underlined its potentially carcinogenic nature. However, there are not many studies regarding the issue. Research in the field of conservation has, in the last few years, focussed on non-toxic inhibitors. Analysing the mechanism corrosion inhibition of BTA on copper covered with corrosion products allows us to understand better the way in which these inhibitors should work and based on this, the direction inhibition research in the conservation field should head.

The demand for non-toxic corrosion inhibitors for corroded copper should start from an understanding of the system copper/corrosion/corrosion products and how different

inhibitive compounds work. Instead of discarding BTA through unexplained or poorly understood shortcomings it is essential to evaluate its mode of action and potential improvement. Research into non-toxic inhibitors has yet to find one which can match BTA in inhibition efficiency in side by side trials.[6] Therefore, the experimental work of this chapter and the analysis of the different BTA compounds using different techniques aimed to comprehend this particular aspect in order to continue testing of other compounds that could be effective inhibitors or could improve the efficiency of BTA.

The results examined largely the diverse beliefs in the field of conservation. BTA is affected by a number of reasons and different application methods can result in different degrees of effectiveness justifying why some professional conservators found BTA effective and others not.

The reason of this study was to understand these factors, not to establish a protocol of practical application for BTA, although the results identify better ways BTA could be used. The next chapter examines the synergistic effect between BTA and other compounds that could lead to better corrosion protection of archaeological copper and copper alloy artefacts.

BTA has been reported to form a complex primarily with copper, however, studies have shown that it can complex with zinc (retarding dezincification of brasses), silver, aluminium and iron. For this reason BTA has been also used as an inhibitor for these

[6] Francois Mirambet, personal communication, Athens, November, 2004. Mr Mirambet conducts research on carboxylates as corrosion inhibitors for copper and iron.

metals. In chapter 7, the inhibition of archaeological copper alloy objects with BTA is examined.

CHAPTER 6

6 Synergistic Effect

6.1 Introduction

Chapter 5 examined benzotriazole (BTA) and selected factors affecting its effectiveness as a corrosion inhibitor for both clean and corroded copper. Analysis of the copper-BTA complex formed on the surface allowed a better understanding of the BTA function and also helped explain its occasional failure to retard corrosion successfully when applied on heavily corroded copper and copper alloys. It has been concluded that reasons behind this failure are closely related to the application methodology as well as the pH of the solution, and to a lesser extent, to the concentration and the solvent.

Based on the results of the initial BTA study, this chapter examines possible synergism between BTA and other compounds with an aim to improve BTA effectiveness as well as to investigate methods that could eventually lead to overall better protection systems for corroded copper.

Six compounds were assessed in combination with BTA. Some of these compounds are known inhibitors for copper and have been tested for archaeological copper (e.g. AMT), others have been tested as copper inhibitors in industry (e.g. PMT, ETH, KEX, BZA) whilst others are not inhibitors but can act synergistically when used with BTA (e.g. KI). The way in which these compounds work either alone or in combination with BTA (based

upon a literature survey is discussed in Chapter 3. Nevertheless, in most cases the results refer to copper that is either corrosion free or is covered only with a thin layer of copper oxide.

The synergistic effect mechanisms observed between different compounds as inhibitors is not always clear or known. However, different inhibition compounds tend to work better when used in combination with other compounds than when used on their own. The definition of a synergistic effect in this context is that the effectiveness of two or more compounds (when used together) is greater than the sum of the effectiveness of each compound alone (*see* Chapter 3).

Each combination of inhibitive compounds was examined by means of a series of experiments and surface analysis. The experiments, as with those discussed in chapter 5, examined factors such as application methodology, solvent and concentration all of which could affect the inhibition process.

Initially experiments using concentrations recommended in the industrial literature for each combination were carried out, these were followed by experiments using higher concentrations of both BTA and the additives taking into account that corroded metals should need higher inhibitor concentration. Each compound was also examined as an inhibitor on each own. The latter was important for comparative and diagnostic reasons especially with regards to the analytical part of the research. Analyses of mixtures can be quite confusing especially if there are too few or no reference data that could be used

comparatively. Another important point is that synergism of inhibitive compound combinations can be proved in relation to the efficiency of each of the compounds used making the individual study of these compounds necessary.

As with the experiments of the previous chapter, the accelerated corrosion testing was designed statistically with Minitab 12.1. The evaluation of the experiments was likewise based on weight change measurement. Tables with the calculated values of inhibitive efficiency are presented and discussed. The effect of the factors and the analysis of the experiments are discussed. The average inhibitive efficiency % of the coupons treated with the tested compounds of each experiment are given. Complete tables of the weight changes, inhibitive efficiency percentage, main factor and interaction plots as well as the full statistical ANOVA analysis of all the experiments carried out are found in Appendix 1. pH levels and colour changes observed in each case were also measured and are presented in this chapter.

Although the experiments were performed on both clean and pre-corroded copper coupons, only those undertaken on pre-corroded coupons are presented in full, as there were no significant differences on the clean coupons after 840 hours of exposure. Nevertheless, colour changes and surface alterations observed on the clean coupons are discussed in detail. Interestingly, some of the compounds tested caused significant colour changes on the clean coupons. Colour measurements using a Minolta colorimeter allowed a more objective evaluation of these changes.

SEM imaging of the treated coupons was of great interest for surface alterations caused by the inhibitive treatments. Some of the changes were not visually with naked eye detectable but under the SEM the results were remarkable. The analyses of treated copper coupons aimed to give possible explanations as to why some treatments work better than others and how certain factors examined affect their performance. The way the different compounds complex with copper and the film formation are of great significance for the treatment efficiency and thoroughly discussed. FTIR and XPS were used to examine the films formed on the surface. The analytical work examined the way that these compounds are bonded to copper and the interaction between them and BTA. FTIR was carried out using transmittance and absorption reflectance mode. XPS and FTIR examined treated surfaces with the aim to understand in full the synergism if any between the selected compounds. The results from the analysis of BTA (see Chapter 5) and any analysis or new compound identification were used as a reference for the analysis of the mixed inhibitor treatments.

Finally, there is a discussion of the experimental results in relation to the analytical findings.

6.2 Accelerated corrosion testing of BTA solutions with additives

The experiments of the possible synergistic effects between BTA plus the six compounds were carried out following a series of experiments. Initially, the inhibitor concentrations recommended in the literature were used in examining the effect of the combined treatment on clean and artificially corroded copper coupons. Following this, more experiments were performed examining several variables that could affect the process. Therefore, the first

series of experiments presented here are those using concentrations already established by other researchers whilst the second set examined five factors in two levels. The factors examined in these experiments were: BTA concentration (0.1 and 0.25M), the presence of second inhibitor, the time of immersion (1 and 24 hours), the RH % the coupons were exposed to after the treatment (60±5 and 95±5%) and finally the copper substrate (clean and corroded coupons). These designs aimed to evaluate factors that were proven to be substantial for the BTA efficiency in Chapter 5. The design used is give in table 6.1. From the results of these experiments it was clear that the RH and the substrate are the more significant factors. It seems that the overall exposure period was not sufficient (840h) to allow evaluation of the treatments of corrosion protection provided to clean coupons treated with the different inhibitors at both RH levels. The 840 hours of exposure were not enough even in case of corroded coupons treated with the different combination of inhibitors when exposed to 60% RH as they did not show significant signs of corrosion.

Table 6.1. Table of experimental design with five factors at two levels

Table 6.2. Table of three-factor design extracted from design showing in table 6.1.

Factor	Level -	Level +
BTA concentration	0.1M	0.25M
2nd inhibitor (AMT, BZA, ETH, KEX, KI, PMT)	No	0.1M
Time of immersion	1h	24h
RH	95±5%	60±5%
Copper Substrate	Corroded	Clean

Factor / Level	Level-	Level +
BTA concentration	0.1M	0.25M
2nd Inhibitor	No	0.1M
Time of immersion	1h	24h

For this purpose the design shown in table 6.1 was simplified from a five factor to a three factor experiment showing in table 6.2. The reason for the exclusion of 60%RH and clean coupons as factors in the discussion of the results gave more space in order to evaluate the

effect of the other factors that were of major importance for this research. The selection and justification of inhibitors and combinations is discussed in chapter 3.

Finally, it is important to discuss the application method followed in all treatments to minimise errors. In many of the inhibitor solutions examined, formation of precipitates on the coupon surface was observed. The formation of precipitates in conservation is removed either by rinsing with a solvent or by swabbing of the surface using cotton swabs soaked in solvent. In this case this could have added one more factor, which is that of surface finishing subject to human dexterity. Also, only some of the solutions presented precipitates and it was imperative not to alter the process in order to avoid both systematic and random human errors during the application process that could lead on biased results.

6.3 BTA and AMT ($C_2H_3N_3S_2$)

AMT has been found to be an effective inhibitor for copper in chloride containing media in very low concentrations. AMT causes a shifting of the corrosion potential into more positive values (Zucchi *et al*, 1996:147-154) and has been reported to be a more effective inhibitor than BTA (see chapter 3). Research has been undergone not only for industrial applications, but also for conservation purposes. Faltermeier (1995), Ganorkar *et al* (1988), and others have found AMT an effective inhibitor for corroded copper.

The aim of these experiments was to examine possible synergism between the two inhibitors. However, comparison between two inhibitors that have been reported to be effective on their own was important and is also discussed. AMT could possibly be a more

effective inhibitor than BTA. AMT has been reported to be a better inhibitor than BTA in short term exposure, long term exposure of coupons treated with BTA and AMT showed that BTA is more effective than AMT (Mohamed *et al*, 2004:369-378). A complete literature review on research regarding AMT is found on chapter 3.

The combination of BTA with AMT has not been tested before. The idea of mixed BTA and AMT solution experiments has been developed by the author based on interest to the individual properties of the compounds.

6.3.1 Experiment BTA+AMT 1

The first experiment examined BTA and AMT at the same concentration in two different solvents in order to assess their effectiveness as inhibitors for copper, as well as the possible synergistic effect between them. The concentration selected was 0.01M because AMT is not easily dissolved at higher concentrations. Both deionised water and ethanol were selected to examine whether the solvent affects the process or not. All of the treatments were carried out on artificially corroded copper coupons. All the coupons remained immersed in the solutions for twenty four hours. The total number of coupons used was 24. The design is shown in table 6.3. The coupons were exposed to 95±5%RH and were monitored at regular intervals.

Table 6.3 Three factors were examined in the third experiment of the AMT and BTA combination.

Factor	Level -1	Level 1
BTA	No	0.01M
AMT	No	0.01M
Solvent	H_2O	EtOH

6.3.1.1 Results BTA + AMT 1

Coupons treated with AMT showed high inhibitive efficiency. AMT in ethanol was more effective than the same concentration in deionised water. Coupons treated with BTA showed uneven results in both solvents used, with accelerated corrosion being predominant. The combination of BTA with AMT resulted in increased efficiency, especially over BTA alone. Although BTA alone did not seem to retard corrosion satisfactorily, when used in combination with AMT the efficiency increased radically.

Table 6.4. Average inhibitive efficiency values of BTA, AMT and BTA + AMT treatments of BTA + AMT 1.

BTA + AMT 1	Inhibitive Efficiency % (Average Values)				
Treatment	24h	48h	168h	504h	840h
BTA 0.01M + AMT 0.01M/EtOH	43.9	17.7	21.6	16.5	11.8
BTA 0.01M + AMT 0.01M/H2O	47.0	15.5	19.6	9.7	10.8
BTA 0.01M/EtOH	-6.7	-8.6	-3.3	-4.2	-3.1
BTA 0.01M/H2O	5.7	5.1	9.7	5.4	5.2
AMT 0.01M/EtOH	51.2	22.5	26.9	20.9	20.4
AMT 0.01M/H2O	18.7	-1.0	3.9	-1.8	-0.8

This experimental result showed there is synergistic effect between BTA and AMT, also that the solvent does not affect this outcome. The inhibitive efficiency of both solutions was similar throughout the monitoring of 840 hours. The average values of AMT efficiency were

The statistical analysis of the experiment showed that AMT is the most significant factor and remains as such throughout the monitoring process. BTA appears initially to be insignificant for the process however, after 168 hours of exposure, it becomes slightly more significant. The solvent is in general insignificant with an exception at 504 hours of

exposure, where there is some effect. The most important interaction is that between BTA and solvent. From the pareto charts, AMT is the most important factor followed by the interaction between BTA and solvent, then BTA and then the interaction between AMT and solvent.

The results showed there is a definite synergistic effect between BTA and AMT. This is more apparent when comparing the low efficiency BTA exhibits in these concentrations with the efficiency of the mixtures of BTA and AMT in both solvents.

6.3.1.2 pH of solution

The pH of the BTA and AMT solutions remained slightly acidic (around 4) this supports the argument of the synergistic effect observed between the two compounds. The failure of BTA to inhibit copper corrosion under certain conditions is attributed to some extent to a pH drop. The slightly acidic values of the combination measured proved that the film formed in the case of BTA and AMT solutions is independent of the pH.

6.3.2 Experiment BTA + AMT 2

Similarly to the previous combinations examined, a second series of experiments using higher BTA concentrations were carried out examining five factors at two levels: the BTA concentration, the time of immersion, the presence of AMT, the relative humidity and the substrate. For the same reasons mentioned above the experiment is presented here simplified, examining three out of the five factors. The factors and their levels are shown in

table 6.5. These experiments were examined at 24, 48, 168 and 504 hours[1]. This confirmed that the substrate and the relative humidity are critical in the corrosion and inhibition processes. Longer periods of time were necessary to assess the performance of the inhibitors at this RH as all of the tested inhibitors performed well. The solvent used in all solutions was ethanol, analar grade. The design used was a full factorial design of three factors at two levels and the total number of corroded coupons used was 24.

Table 6.5. Factors and the levels examined in the second experiment of BTA and AMT.

Factor	Level -1	Level +1
BTA concentration	0.1M	0.25M
AMT	No	0.01M
Time of immersion	1h	24h

6.3.2.1 Colour alterations BTA + AMT 2

Clean copper coupons treated with the different solutions of BTA with AMT kept their metallic appearance. A film was formed on the surface which altered slightly the appearance of the coupon by adding a slightly darker reddish tint. No differences where observed between the coupons treated for one hour and those treated with the solutions for 24 hours. At higher concentrations, a whitish precipitate (a tide line from drying) was evident on the surface of some of the coupons treated with BTA 0.25M and AMT 0.01M for twenty four hours.

[1] Unfortunately, due to a technical problem with the environmental chamber, the monitoring had to stop after 504 hours of exposure.

Corroded coupons treated with BTA and AMT solutions did not present any great colour alterations. More specifically, coupons treated with 0.1M BTA and 0.01M AMT in both water and ethanol did not present any changes. In the case of coupons treated with 0.25M BTA with 0.01M AMT in ethanol there was a slight darkening of the surface and in some case of twenty four hour treatment, there was also some pale green precipitate on drying. Interestingly, these treatments exhibited less colour alterations than BTA alone.

6.3.2.2 Results of BTA + AMT 2

The results showed that the coupons treated with the mixtures of BTA and AMT exhibited the higher inhibitive efficiency. All of the BTA with AMT performed better than BTA and AMT on their own. Table 6.6 shows the average values of inhibitive efficiency of the solution tested. The tables showing the weight uptake and inhibitive efficiency of all the coupons are in Appendix 2.

The most effective treatments were found to be the solutions of 0.1M BTA + 0.01M AMT in both periods of immersion (one and twenty four hours). The solutions of 0.25M BTA + 0.01M AMT also performed well especially the coupons treated for an hour with the solution. In the latter solution the longer immersion into the solution resulted in decrease in the effectiveness of the treatment.

Interestingly, although the efficiency of BTA when used alone is affected by the concentration, with treatments using 0.25M being more effective than those of 0.1M, when AMT is added to the solution, the lower % solution is proven to be more effective. Another

interesting outcome of this experiment is that the immersion time does not affect dramatically the treatment. In Chapter 5, the effectiveness of BTA was largely affected by the time the coupons remained into the solutions. The longer the coupons stayed the less effective the treatment was proven to be and in some cases (0.1M BTA in deionised water) the effect was remarkable as it resulted in accelerated corrosion. The presence of AMT in the BTA solution clearly showed that the treatments were unaffected by the immersion with the exception of 0.25M + 0.01M AMT and that after twenty four hours of immersion.

The statistical analysis of the experiment showed that the most important factor in the process was the presence of AMT in the solution. The effect of AMT in the BTA solution resulted in a positive outcome. BTA concentration and time of immersion were insignificant for 168 hours. After 504 hours of exposure, immersion becomes the most significant factor and BTA concentration also becomes relatively important for the process. The results should be viewed in relation to the inhibitive efficiency of all of the treatments tested. The results of the statistical analysis are characteristic for the importance of the time of immersion not in the mixtures of BTA + AMT, but to BTA only solutions.

Table 6.6. Average values of inhibitive efficiency of AMT and BTA treatments of experiment 2.

BTA+AMT 2	Inhibitive Efficiency % (Average values)			
Treatment	24h	48h	168h	504h
BTA 0.1M, 1h	24.1	19.9	11.7	11.3
BTA 0.1M, 24h	19.7	14.5	10.1	3.2
BTA 0.1M + AMT 0.01M, 1h	82.3	71.4	51.0	13.8
BTA 0.1M + AMT 0.01M, 24h	90.8	70.8	55.9	17.2
BTA 0.25M, 1h	36.8	35.0	31.3	23.3
BTA 0.25M, 24h	32.0	26.2	20.6	8.5
BTA 0.25M + AMT 0.01M, 1h	77.2	57.6	43.1	11.8
BTA 0.25M + AMT 0.01M, 24h	68.2	60.6	44.1	10.6

Table 6.5 shows the average inhibitive efficiency values of the treatments examined. All of the BTA and AMT treatments show increased effectiveness when compared to those of BTA alone.

The period the coupons stay immersed in the solution is a factor interacting with BTA, resulting in lower inhibitive efficiency when the coupons are treated in the BTA solutions for longer, which is in agreement with the results of the experiments presented in Chapter 5. However, time of immersion is not as significant for the combination of BTA and AMT. The weight changes in all four combinations are too close to be able to consider substantial differences. Still, the combination that seems to work best is that of 0.1M BTA with 0.01M AMT at both treatments (one and twenty four hours).

The analysis of the experiment also showed that there are two-way interactions between BTA and AMT and BTA and time of immersion at all monitoring intervals. Although there is no interaction between AMT and immersion up to 168 hours of exposure, there is strong interaction between them after 504 hours. It seems that after some time the change from one to twenty four hours of immersion affects AMT which in turn affects BTA. There seems to be interaction between all three factors at 504 hours.

6.3.3 Experiment BTA + AMT 3

Based on the results of the previous experiment, where the time of immersion was not found to be a significant factor, it was decided to continue the testing of BTA with AMT using one hour of immersion. Furthermore, because the increase in BTA concentration was

not found significant it was decided to test whether even lower BTA concentration would inhibit corrosion effectively when used in combination with AMT.

Table 6.7. Factors examined in the third experiment of BTA and AMT combination.

Factor	Level -	Level +
BTA concentration	0.01M	0.1M
AMT	No	0.01M
Solvent	Water	Ethanol

The factors examined in this set of experiments were the BTA concentration, the presence of AMT and the solvent and are shown in table 6.7. Table 6.8 shows the average efficiency at 24, 48, 168, 504 and 840 hours of exposure. The most effective treatments were once more those of BTA with AMT.

6.3.3.1 Results of BTA + AMT 3

The coupons treated with BTA and AMT solutions in both deionised water and ethanol presented higher inhibitive efficiency than those treated with BTA solutions. The treatment of coupons with 0.01M BTA in both water and ethanol resulted mostly in acceleration of the corrosion rate as two out of three coupons in each treatment gained more weight than the untreated coupons. A similar result was observed on coupons treated with 0.1M BTA in deionised water, where the coupons exhibited accelerated corrosion. The treatment of 0.1M BTA in ethanol provided protection by 20% on average after 24 hours of exposure which dropped to 6% after 840 hours.

However, even though BTA in lower concentrated solutions or when dissolved in water did not provide any protection to the corroded coupons, the addition of AMT into these BTA solutions resulted in increased efficiency. The most effective treatment was found to be the solution of 0.1M BTA + AMT in ethanol which was over 85% effective after the 24-hour exposure and remained the most effective treatment throughout the monitoring.

The solutions of 0.1M BTA + 0.01M AMT in water, 0.01M BTA and 0.01M AMT in ethanol and 0.01M BTA + 0.01M AMT in water followed also exhibited high effectiveness. An interesting point is that although the efficiency of the latter two treatments was similar for the first 168 hours of exposure, after that the ethanol behaved better than the aqueous solution. This observable fact can be seen in table 6.8 that shows the average inhibitive efficiency values of the BTA + AMT treatments tested in experiment 3.

Table 6.8. Average inhibitive values of BTA and BTA + AMT treatments.

BTA + AMT 3	Inhibitive Efficiency % (average values)				
Treatment	24h	48h	168h	504h	840h
BTA 0.01M/H2O	6.9	14.4	9.7	6.4	7.2
BTA 0.01M/eth	-5.3	-4.0	-3.3	-3.1	-1.0
BTA 0.01+AMT/H2O	47.7	41.5	19.6	10.7	12.6
BTA 0.01+AMT/eth	44.6	38.9	21.6	17.4	13.6
BTA 0.1M/H2O	-7.8	-5.2	-2.7	-2.3	2.3
BTA 0.1M/eth	19.5	17.9	9.6	2.6	6.2
BTA 0.1M +AMT/H2O	57.2	51.3	30.6	11.3	3.7
BTA 0.1M +AMT/eth	87.0	75.0	60.3	17.7	15.2

From the statistical analysis of the experimental results it was found that the most significant factor affecting inhibitive efficiency was again the presence of AMT into the BTA solutions which resulted in increased efficiency. The BTA concentration and the solvent were found to be almost insignificant in the overall process examined.

The most important interaction is that of BTA with the solvent, followed by the interaction between BTA and AMT. The pareto charts showing the overall importance in the process including main factors and interaction factors illustrated that the most important factor is indeed the presence of AMT, followed by the interaction between BTA and solvent, the BTA concentration and the interaction between BTA and AMT.

As a conclusion there is synergistic effect between BTA and AMT as it was proved by the experiments assessing their efficiency. In all cases the efficiency of the BTA-AMT solutions were greater than the efficiency of BTA or AMT alone.

6.4 Benzotriazole and Benzylamine (C_7H_9N)

Benzylamine (BZA) although not an effective inhibitor was found to improve the BTA efficiency because of the synergistic effect observed between them. The addition of BZA in to the BTA solution affects the kinetics of the film formation. The film formed is a Cu(II)BTA polymer (Fleischmann *et all*, 1985: 1591-1602).

A series of experiments were undertaken to examine the synergistic effect between BTA and BZA. BZA is an amine with alkaline pH (≈11). The addition of BZA into the BTA

solution also affects the pH which is modified to slightly alkaline levels. Therefore, apart from the effect that BZA has on the film growth, it is expected to assist BTA in other ways.

6.4.1 Experiment BTA + BZA 1

The first experiment examined concentrations and conditions close to those already tested on clean copper for industrial purposes. The aim of the testing was to examine if the suggested synergistic effect between BTA and BZA also happens when applied on artificially corroded copper coupons resulting in increased inhibitive efficiency. The treatments were applied also on clean copper coupons but since they did not present any weight change, the results of the corroded coupons are mainly discussed here.

The two factors tested were BTA and BZA as shown in table 6.9. The inhibitors were dissolved in deionised water. The 2^2 full factorial design used allowed the evaluation of the effectiveness of each compound on its own as well as the effectiveness of the treatment when the compounds are used together. The total number of coupons tested was 24. The pH of all the solutions was measured before and after the immersion of the copper coupons. Although Fleischmann *et al* (1985) adjusted the pH to 7 using different chemicals, this was not carried out because chemicals such as HCl could accelerate copper corrosion.

Table 6.9. Experimental design used for the testing of the combination of BTA with BZA (exp. 1).

Factor	Level -	Level +
BTA	No	0.021M
BZA	No	0.023M

6.4.1.1 Colour changes BTA + BZA 1

Both solutions were initially clear. BZA appeared semi-opaque with a light green sediment soon after the immersion of the coupons. Similarly, BTA also presented green sediment after the immersion. The corroded coupons treated with BTA did not present any significant colour changes, whilst the coupons treated with BZA turned green.

6.4.1.2 pH

The pH of the BZA solution was around 11, in combination with BTA it was around 8. The pH of the BZA solution dropped slightly (from 10.8 to 10.2) whilst the pH value of the solution of the two inhibitors together remained the same even after the immersion of the coupon. The pH values are given in table...

6.4.1.3 Results of BTA + BZA 1

The results showed that BZA is not an effective inhibitor by itself. Quite the opposite, all of the coupons treated with BZA gained more weight than the control untreated copper coupons, resulting in increased corrosion rate. The more successful treatment is that of BTA 0.021M which exhibited an inhibitive efficiency that varied from 16 to 46% after 24 hours of exposure. The higher value was not considered representative of the treatment. The combination of BZA and BTA did not increase the inhibitive efficiency. On the contrary, their combination was found to be less effective than BTA alone. As can be seen in table 6.10 two out of three coupons gained more weight than the untreated copper coupons, indicative of the accelerated corrosion they have undergone.

Table 6.10. Average Inhibitive Efficiency % values of BTA and BZA treatments of BTA+BZA 1.

BTA+BZA 1	Inhibitive Effiiency%				
Treatment	24h	48h	168h	504h	840h
0.021M BTA	26.6	27.8	16.8	22.4	21.7
0.021M BTA +0.023M BZA	-3.1	0.5	-8.2	-0.9	0.4
0.023M BZA	-11.9	-10.3	-17.3	-9.4	-18.3

From the coupons treated with the combination of BTA with BZA, two out of three gained more weight than the untreated coupons, while the third gained less than the untreated, still even the third coupon presented lower efficiency than BTA alone (average value 7%).

The statistical analysis of the experiments showed that BTA is the factor that is significant for the overall process with BTA being present in the solution resulting in a positive effect. BZA is less significant, its presence has a negative effect. There is also interaction between the BTA and BZA, the change of values of one factor affecting the other. The significance of the factors and their effects as well as the interactions observed were consistent in all monitoring time intervals (24-840 hours of exposure).

From the analysis of variance and the pareto charts it is interesting to note that in most monitoring intervals the interaction between the BTA and BZA was the most important for the overall inhibition process, followed by BTA. It is once more confirmed that BZA on its own is not an important variable.

From the results it was clear there was no synergism between the two compounds. However, because the concentrations used could possibly be very low for corroded copper,

the next experiment examined whether more concentrated solutions of these compounds could demonstrate the synergistic effect of the compounds.

6.4.2 Experiment BTA + BZA 2

Following the results of the previous experiment using concentrations already tested as well as the results of the experiments about BTA efficiency (*see* Chapter 5), the testing of BTA solutions with BZA continued using not only higher concentrations but also different solvent (i.e. ethanol). The reason behind experiments using higher concentrations of the compounds is that in theory, higher concentration results in greater inhibitive efficiency. Similarly, corroded copper needs higher concentration of inhibitors than clean copper (Sastri, 1996).

The aim of this experiment was to assess whether more concentrated solutions of BTA and BZA could result in greater inhibitive efficiency, proving that there is a synergistic effect between the compounds as suggested in the literature. The factors examined were the BTA concentration (using the concentrations tested in Chapter 5), the presence of BZA also in higher concentration (0.1M), the time of immersion (one and twenty-four hours), the relative humidity (60 and 95%) and the substrate (clean and corroded copper). 0.25M BTA was selected as the concentration commonly used in conservation of metals. Ethanol was selected as solvent because BTA is not soluble in water at higher concentration (0.25M). The factors tested and the levels of the experiment used and discussed are found in table 6.11.

Table 6.11. Simplified three factor design discussed as experiment 2. Because RH and substrate were proven to be the most significant factors, the design was re-organised into a 2^3 factorial design that would allow the evaluation of the synergism between the factors and the effect of the time of immersion

Factor	Level -	Level +
BTA concentration	0.1M	0.25M
BZA	No	0.1M
Time of immersion	1h	24h

The total number of coupons used for this experiment was 96. The coupons exposed to RH 60±5% did not present any significant weight changes, as the time of exposure (504 hours) was not sufficient to assess the treatments. The clean coupons did not show either any great differences in weight after exposed to high relative humidity, therefore the results presented here are those for the corroded coupons, exposed at 95±5%RH. For this purpose the experiment was re-arranged removing two out of five factors in order to have meaningful results. The experiment was examined as a three factor experiment that included 24 coupons. The new design is given in table 6.11. [2]

6.4.2.1 Colour changes

Clean coupons treated with the solution of 0.1M BTA + 0.1M BZA in ethanol for an hour were covered with a film that did not cause any significant colour changes. The metallic copper appearance was retained although there were some white inhibitor crystals formed on the surface. After twenty four hours of immersion, the coupons were covered with a semi-transparent non-uniform light green film and had almost lost their metallic appearance. The coupons treated with the solution of 0.25M BTA + 0.1M BZA for an hour

[2] The coupons were exposed for 840 hours in total, however, after the 504 hour exposure at 95±5% RH there was an unfortunate breakdown of the chamber and for reliability purposes the results are presented only up to 504 hours. The same applies for all the second experiments of the combinations (i.e. AMT 2, BZA2, ETH2, KEX2, KI2 and PMT2).

although had some light green sediment and some inhibitor crystals formed throughout the surface of the coupons, did not present great colour changes and they retained their metallic appearance. However, the coupons treated for twenty four hours were covered with a light green semi-opaque film, thicker than that observed in the previous treatment. The thickness varied, on the underside (where the inhibitor was for longer during drying) the film was thicker and the coupon was totally covered without any metal evident underneath. As a conclusion, colour changes of copper treated with the mixture of BTA with BZA are dependent on the concentration of the solution as well as the time of immersion (Fig. 6.1).

Corroded copper coupons treated with the combination of BTA + BZA presented generally a slight darkening of the surface. Coupons treated with 0.1M BTA + 0.1M BZA for an hour presented smaller changes. The cuprite colouration was retained although there was a green tint on the surface. After twenty four hours of immersion, the coupons presented a green precipitate on top of the cuprite. Coupons treated with the solution of 0.25M BTA and 0.1M BZA for an hour presented a darker brown colouration and in some cases there was a green precipitate. The same alterations were observed after twenty four hours of immersion. Colour changes observed on coupons treated with BTA solutions were discussed in full in chapter 5.

6.4.2.2 Results of BTA + BZA 2

The substrate and the RH are the most significant factors governing the corrosion of a metal and this is what the results for clean copper show. Clean copper treated with the tested solutions did not present any differences in terms of weight change. Similarly none of the

clean and corroded coupons exposed to 60% RH showed any differences even after 840 hours of exposure.

Table 6.12. Average values of IE% of treated corroded coupons.

BTA-BZA, Exp 2	Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h
BTA 0.1, 1h	24.1	19.8	15.3	14.3
BTA 0.1, 24h	19.7	14.3	11.4	4.0
BTA 0.1+BZA, 1h	-13.6	-10.1	-6.3	-6.2
BTA 0.1+BZA, 24h	-14.5	-9.7	-6.3	-5.1
BTA 0.25M, 1h	36.8	35.0	32.2	24.2
BTA 0.25M, 24h	32.0	26.2	21.6	9.5
BTA 0.25+BZA, 1h	-15.4	-10.1	-8.2	-7.3
BTA 0.25+BZA, 24h	-15.8	-10.5	-7.1	-3.3

Table 6.12 shows the average values of the inhibitive efficiency of the tested treatments applied on corroded copper coupons. The results showed that the most effective treatment was that of BTA 0.25 M followed by BTA 0.1 M. The results of BTA were similar to those of chapter 5. The coupons treated with the combinations of BTA and BZA at different times of immersion showed that there is no synergism between the inhibitors. On the contrary the corrosion rate is greater than that of the untreated control coupons, showing that the combination of these inhibitors instead of acting synergistically to improve the effectiveness of each compound had the opposite effect, accelerating corrosion. The results are in agreement with those of experiment 1 of the same combination, proving that the concentration, time of immersion and solvent examined in this experiment do have a positive outcome in the inhibition process. The reason behind the inefficiency of the combination will be examined later in the analytical part of this chapter.

From the statistical analysis of the results it was found that the presence of BZA is the most significant variable affecting the process. Its presence resulted in increased weight uptake for the coupons, therefore decreased inhibitive efficiency. The BTA concentration and the time of immersion appear relatively insignificant in this experiment since the effect of BZA is so substantial. However, similarly to the results of chapter 5, the increase in concentration resulted in slightly less weight uptake, and consequently increased efficiency, whilst the increase of the periods of time of immersion had the opposite result where longer periods of immersion resulted in decreased efficiency. The results were consistent throughout the monitoring.

There is interaction between BTA and BZA in all monitoring intervals. However, this interaction resulted in negative results in the efficiency. There are no other significant interactions between the other factors, except possible interaction of BZA with time of immersion after 504 hours of exposure.

6.5 BTA and ETH (C_2H_7NO)

Ethanolamine (ETH) similarly to BZA is an amine that added to the BTA solution assists in the film growth kinetics at the same time adjusting the pH to neutral values (see Chapter 3). The synergistic effect between BTA and ETH was examined in this experiment by assessing these two factors BTA and ETH using concentrations recommended in the literature. The solvent used was deionised water.

Table 6.13. Two factor design used for experiment 1 of BTA and ETH.

Factor	Level -	Level +
BTA	No	2.5×10^{-6} M[3]
ETH	No	1.8×10^{-6} M

All the treatments were applied on artificially corroded coupons. The experiment examined two factors (BTA and ETH) at two levels, (where in level -1 the value of each inhibitor was 0) in order to assess not only the interaction between the two compounds but also the efficiency of each compound on their own. Table 6.13 shows the factors and the levels.

Colour observations BTA + ETH

All the solutions were initially clear. However, when the corroded coupons were immersed into the ETH solution there was immediate diffusion from the coupon to the solution which turned quickly from clear to purple.

6.5.1.1 pH

The pH of ETH was found to be 9.5 and that of BTA around 5.1. The pH BTA + ETH was found to be around 9.1. At higher concentrations (0.1M) the pH of ETH was found to be 11 which dropped to 10.7 and 10.6 after the immersion of copper. The pH of BTA was 5.8 which dropped to 4.2 and 3.6 after one and twenty four-hour immersion. The pH level of 0.1M BTA + 0.1M ETH was 9.6 and remained at the same level after copper immersion.

[3] 1 ppm = 1.000000e-06 mol (source: http://www.chemie.fu-berlin.de/chemistry/general/units_en.html)

6.5.1.2 Results BTA + ETH 1

The coupons treated with ETH presented a very different picture than that previously observed on treated corroded coupons. The surface of the coupons was partly etched, removing part of the corrosion layer and leaving a porous metallic surface which had an iridescent purple colour. Although the concentration was relatively low, the dissolution of the corrosion layers makes ETH unsuitable for use on archaeological copper and copper alloys where corrosion is part of the original object. The results of the experiments presented a great variation that does not allow one to draw comprehensive conclusions. BTA showed very high inhibitive efficiency after the 24-hour exposure which dropped considerably after 48 hours of exposure. One of the three coupons (coupon 86) treated with BTA flaked immediately after the twenty four hour exposure to high RH so the weight measure was lower than the original therefore the efficiency values were higher than they should have been. Table 6.14 shows the efficiency of the treated coupons and demonstrates the deviation of the results.

Table 6.14. Table with inhibitive efficiency values of coupons treated with BTA, ETH and BTA-ETH, experiment 1.

BTA and ETH experiment 1	Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h
BTA 2.5 * 10^{-6}M	79.8	14.6	32.5	33.0	22.1
BTA 2.5 * 10^{-6}M	84.7	61.1	38.2	34.8	34.5
BTA 2.5 * 10^{-6}M	1.9	19.9	20.0	24.2	26.5
ETH 1.8* 10^{-6}M	40.1	42.0	40.0	40.3	38.9
ETH 1.8* 10^{-6}M	-25.8	7.2	6.6	11.9	14.8
ETH 1.8* 10^{-6}M	27.8	32.6	32.3	34.3	34.9
BTA 2.5+ ETH 1.8* 10^{-6}M	18.6	17.7	16.3	19.6	22.1
BTA 2.5 + ETH 1.8* 10^{-6}M	47.5	48.7	44.3	44.5	40.2
BTA 2.5 + ETH 1.8* 10^{-6}M	95.1	51.1	44.4	42.4	40.8

Although the results showed that both BTA alone and BTA with ETH exhibit high inhibitive efficiency because the values were highly distributed, conclusions are not easily drawn. For example, after 24 hours of exposure to 95±5%RH, the BTA efficiency varied from 1.9% to almost 85%, the efficiency of ETH varied from -25% meaning corrosion instead of inhibition to 27% and then 40%. Finally the values of BTA with ETH varied from 18 to 95%.

The high inhibitive efficiency of the combination of BTA with ETH might be due to similar phenomena to those observed on coupons treated with ETH alone with the partial etching of the surface and even though the results of this experiment might appear promising, the variations of the values showed that the protection provided might not be as stable as is desirable, or that they might be due to uneven dissolution of corrosion products. More experiments were necessary to assess this.

The analysis of the experimental design showed that after 24-hour exposure to 95±5% RH, BTA is the most important factor whilst after 48 hours of exposure both BTA and ETH are significant for the inhibition process. BTA is more effective when used alone after 24 hours of exposure, but after 48-hour exposure the combination of BTA + ETH performs better than BTA alone.

6.5.2 Experiment BTA + ETH 2

The second series of experiments, examined a higher concentration of the tested compounds in relation with the time of immersion. Similarly to experiment 2 of the previous combination tested, the original experiment included five factors (BTA, ETH,

time of immersion, RH and substrate) with results indicating that the most important factors were the RH and the substrate. In order to evaluate the synergistic effect between BTA and ETH the experiment was subdivided into a smaller one with three factors (BTA, ETH and time of immersion) at two levels. The effect of these factors are examined in relation to corroded coupons when exposed to 95±5%RH. The factors and their levels are shown in table 6.15.

Table 6.15. Factors and the values of levels used for experiment 2 of BTA and ETH.

Factor	Level -	Level +
BTA	0.1M	0.25M
ETH	No	0.1M
Time of Immersion	1h	24h

6.5.2.1 Colour changes

Clean coupons treated with a mixture of BTA and ETH presented different appearances depending mainly on the time of immersion and less on the composition. More specifically, coupons treated with 0.1M BTA and 0.1M ETH for 1h and 0.25M and 0.1M ETH for 1 hour kept their metallic appearance. The surface lost its shine and become slightly duller. In the latter there was also some whitish precipitate on the surface (Fig. 6.2).

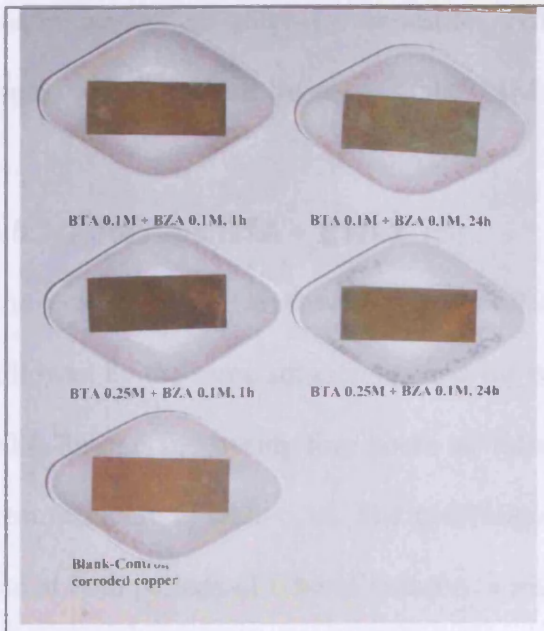


Figure 6-1. Corroded copper coupons treated with BTA +BZA solutions (see experiment BTA+ BZA 2).

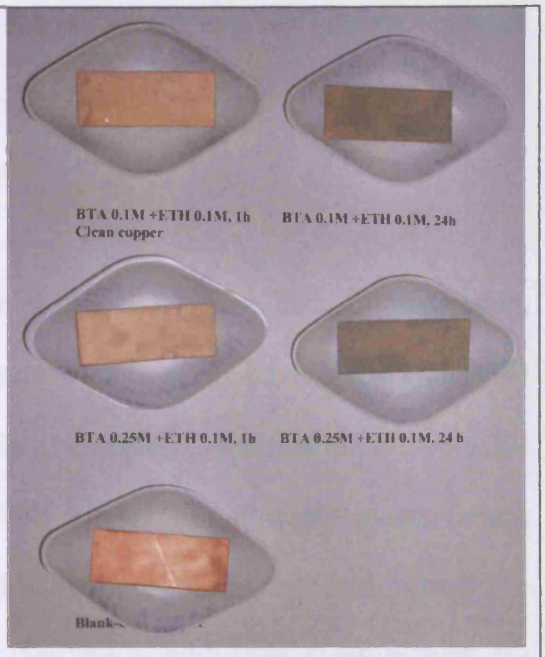


Figure 6-2. The time of immersion affected the film formed on copper coupons treated with BTA+ETH treatments. Longer time of immersion resulted in the formation of a semi-opaque green film on the surface.

Coupons treated with the same solutions for 24 hours lost their metallic appearance. They were covered with a green film. In case of 0.1BTA with 0.1M ETH the film appeared to be homogeneous, whilst when in case of 0.25M with ETH the film did not appear uniform, with some thicker precipitates formed on the surface.

The surface of the corroded coupons treated with 0.1M BTA + 0.1M ETH for both 1 and 24 hours of immersion appeared to have a green/brown film covering the surface which appeared to be on top of cuprite originally found on the surface of the coupons. The coupons treated with 0.25M + 0.1M ETH for an hour had less colour alteration than those treated for 24 hours. More specifically, when the time of immersion was one hour, the cuprite colouration of the surface was retained although darker and with some green

precipitate due to solvent evaporation. After 24 hour immersion, the coupon appeared green, similar to those treated with the 0.1M BTA + 0.1M ETH solution.

6.5.2.2 Results BTA + ETH 2

The most effective treatment was found to be 0.25M BTA, one hour of immersion, followed by the same solution applied for twenty four hours of immersion, and then 0.1M BTA for one and twenty four hours of immersion. The average values of the BTA + ETH treatments are in table 6.16. The combination of BTA + ETH in all tested concentrations and at both periods of time of immersion resulted in acceleration of the corrosion rate. The fact that BTA treatments were more effective than the combination together with the increased corrosion showed that there is no synergism between the two compounds.

Table 6.16. Average values of inhibitive efficiency of BTA + ETH treatments of experiment 2.

BTA + ETH 2	Inhibitive Efficiency % (Average Values)			
Treatment	24h	48h	168h	504
BTA 0.1M, 1h	24.1	19.9	11.7	11.3
BTA 0.1M, 24h	19.7	14.5	10.1	3.2
BTA 0.1M + ETH 0.1M, 1h	-29.5	-18.9	-11.9	-6.9
BTA 0.1M + ETH 0.1M, 24h	-29.2	-22.7	-15.4	-10.3
BTA 0.25M, 1h	36.8	35.0	31.3	23.3
BTA 0.25M, 24h	32.0	26.2	20.6	8.5
BTA 0.25M + ETH 0.1M, 1h	-30.3	-20.5	-10.6	-3.5
BTA 0.25M + ETH 0.1M, 24h	-23.4	-19.7	-14.2	-6.4

In terms of factor analysis, the presence of ETH was found to be the most significant factor in the experiment and it remained as such throughout the monitoring period. Its effect was however negative since the coupons treated with the combinations of BTA with ETH gained more weight than not only those treated with BTA but also than the untreated coupons. The time of immersion and the BTA concentration after 24 hours affected the process only slightly with higher BTA concentration being more efficient. After 48-hour

exposure, the results indicate that the coupons that had stayed immersed for one hour were more protected than those immersed for 24 hours. At 168 and 504 hours of exposure, the time of immersion became totally insignificant.

BTA and ETH interact but again the most important interaction was found to be that of BTA with time of immersion.

From these two experiments it was found there is no synergistic effect between BTA and ETH. The fact that ETH dissolved part of the corrosion products found on the surface makes it unsuitable for use on archaeological objects.

6.6 BTA and KEX ($KC_3H_5S_2O$)

Potassium ethyl xanthate (KEX) has been used in industry in separating the mineral from ores in the floatation process. On the basis that floatation processes are electrochemical in nature and comparable to those of corrosion and corrosion inhibition, KEX has also been studied as corrosion inhibitor for copper with satisfactory results in chloride containing environments. KEX adsorbed on the copper surface alters its properties from hydrophilic to hydrophobic (Souto *et al*, 1997:508-511). This combination was assessed with three experiments.

6.6.1 Experiment BTA + KEX 1

The first series of experiments examined if BTA with KEX work synergistically to inhibit copper corrosion. The inhibitor concentrations used were those recommended in the literature. This experiment allowed the evaluation of BTA and KEX as inhibitors on their

own. The solvent used was deionised water. The factors and their levels are shown in table 6.17.

Table 6.17. Design used for experiment 1 of BTA and KEX applied on corroded copper coupons. The solvent used was deionised water.

Factor	Level -	Level +
BTA	No	0.001M
KEX	No	0.01M

The KEX solution was clear but slightly yellow. After one hour of immersion the coupons were covered with loose yellow sediment. The solution of BTA and KEX was also clear and slightly yellow.

6.6.1.1 pH

The pH of the solution was around 7.4 and did not change after the one and twenty four-hour immersion of copper.

6.6.1.2 Results of BTA + KEX 1

The results showed that KEX was the most efficient of the treatments tested with average IE 36% over 23% of the KEX+BTA combination and 9.7% of BTA at 24 hours of exposure (table 6.18). The low inhibitive efficiency of BTA might be due to the low concentration (0.001M) or the solvent (deionised water). The combination of BTA with KEX although did not improve the KEX efficiency, however, it improved the BTA efficiency for the first 168 hours of exposure. At 504 and 840 hours of exposure to high RH, BTA performed better than BTA with KEX. Still the difference between these treatments at 504 and 840-

hour exposures are too small to draw comprehensive conclusions as to whether a synergistic effect between the two compounds exists or not.

Table 6.18. Average values of inhibitive efficiency of BTA, BTA+ KEX and KEX treatments of experiment BTA + KEX 1.

BTA + KEX 1	Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h
BTA 0.001M	9.7	9.6	7.1	17.0	16.3
BTA 0.001M+KEX 0.01M	23.3	25.5	13.8	13.8	13.0
KEX 0.01M	35.5	34.2	21.0	22.1	21.2

The analysis of the experiment showed that the most significant factor is KEX and remained as such throughout the exposure. BTA is insignificant for the first 168 hours of exposure. After 504 hours of exposure BTA becomes somewhat significant, still not as important as KEX. Another interesting aspect is that the presence of BTA into the KEX solution had a negative effect on the overall inhibition process. These agree with the values explained earlier where KEX is more effective than its combination with BTA. At 48 and 168-hour exposure, the presence of BTA is totally insignificant, whilst at 504 and 840-hour exposure, the presence of BTA had a positive effect on the process. In terms of interactions, the two factors clearly interact throughout the monitoring process.

The results of this experiment are inconclusive as they change over time of exposure. The concentrations used were very low however, these were originally meant to be used on clean copper, not corroded like the case here. These concentrations being so low were probably under the optimum range required for corroded copper, therefore the experiments with BTA and KEX continued.

6.6.2 Experiment BTA + KEX 2

Similarly to the previous compounds tested, the second experiment of this combination examined the combination of BTA with KEX and their potential synergism in the copper corrosion inhibition at higher concentrations. Similarly, the original design included two more factors, RH and copper substrate but was subdivided into a three factor design shown in table 6.19. These factors were BTA concentration (0.1M and 0.25M), the presence of KEX in the BTA solution or not but in higher concentration (0.1M) and the period of the time of immersion (1 and 24 hours). The solvent selected for all the solutions was ethanol, analar grade, as 0.25M BTA is not soluble in water. The total number of coupons used was 24. The results of the clean copper coupons and those exposed at 60% RH are not discussed here for the same reasons explained earlier on.

Table 6.19. Design of experiment 2 for BTA and KEX on corroded coupons.

Factor	Level -	Level +
BTA	0.1M	0.25M
KEX	No	0.1M
Time of Immersion	1h	24h

6.6.2.1 Colour changes

All of the clean copper coupons treated with the mixture of BTA with KEX lost their metallic appearance. The surface was covered with a thick, dark green/black film. Both the time of immersion and the concentration affected the thickness of the film consequently the appearance of the coupons. More significant of the two factors seems to be the time of immersion for the colour alterations. Coupons treated with 0.1M BTA and 0.1M KEX for an hour were covered with a thin dark, and, in some parts iridescent, film. Coupons treated for 24 hours totally lost their metallic appearance and were covered with a dark green/black film which appeared flaky in some parts. Coupons treated with 0.25M BTA and 0.1M KEX

presented a similar picture. The coupons treated for an hour were covered with a thin black film that resulted in loss of the metallic appearance. The coupons treated with the same solution for 24 hours were also covered with a black flaky film resulting in loss of their metallic appearance. The extent of the flaking was such that it exposed underneath this flaky layer the metal surface itself covered with a thinner dark (almost black) film, similar to that formed on the surface after an hour of immersion (see figure 6.3).

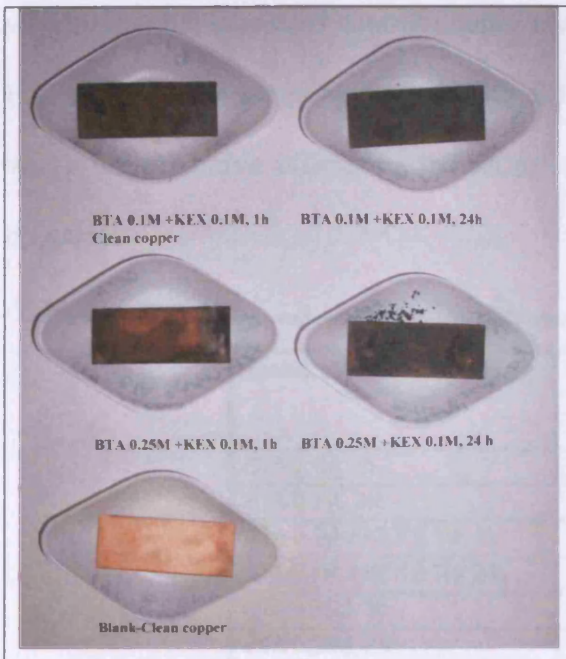


Figure 6-3. Clean copper coupons treated with BTA + KEX solutions lost their metallic appearance after the treatment. The film is also flaky after 24-hour immersion.

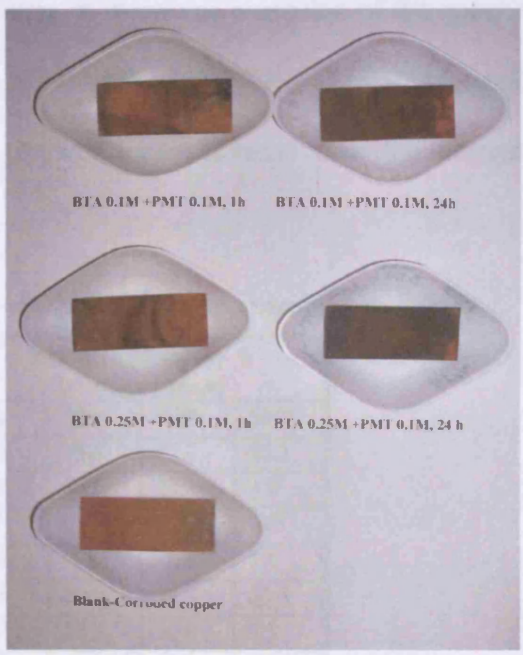


Figure 6-4. Corroded copper treated with BTA + PMT solutions.

Corroded copper coupons treated with BTA with KEX exhibited great colour alteration with all solutions. The coupons treated with 0.1M BTA and 0.1M KEX for an hour were covered with a dark green/black layer. The film appeared uniform with areas of black precipitate. After twenty four hours of immersion, the coupons were covered with a layer of similar dark green/black colouration, which appeared to be flaky. There were also some green tidelines left from solvent evaporation. Coupons treated with 0.25M BTA and 0.1M

KEX for an hour were also covered with a dark green layer with tidelines. A similar picture was observed after twenty four hours of immersion. In both solutions the film appears thicker at longer periods of time of immersion.

6.6.2.2 Results BTA + KEX 2

All the coupons treated with the different solutions of BTA and KEX gained a lot more weight than the untreated control coupons resulting in increased corrosion of the coupons. For example, the coupons treated with 0.1M BTA with 0.1M KEX exhibited negative values of inhibitive efficiency indicating the greater mass increase than the untreated coupons.

Table 6.20. Average values of inhibitive efficiency of BTA and KEX treatments of experiment 2.

Treatment	Inhibitive Efficiency % (average values)			
	24h	48h	168h	504h
BTA 0.1M, 1h	24.1	19.9	11.7	11.3
BTA 0.1M, 24h	19.7	14.5	10.1	3.2
BTA 0.1M + KEX 0.1M, 1h	-7.7	-5.2	-7.6	-6.0
BTA 0.1M + KEX 0.1M, 24h	-9.6	-1.3	-1.1	1.4
BTA 0.25M, 1h	36.8	35.0	31.3	23.3
BTA 0.25M, 24h	32.0	26.2	20.6	8.5
BTA 0.25M + KEX 0.1M, 1h	-2.4	-1.6	-6.9	-8.5
BTA 0.25M + KEX 0.1M, 24h	-22.7	-17.1	-14.7	-13.7

The coupons treated with 0.25M BTA and 0.1M KEX in ethanol, for twenty four hours, presented the higher mass increase, representing the higher corrosion rate of this experimental group. The prolonged immersion of the coupons in the inhibitive solution had a negative effect in the overall process. Table 6.20 shows the average inhibitive efficiency % values as calculated from these weight measurements.

As a result, the treatments of corroded coupons with mixtures of BTA with KEX in these concentrations caused a considerable increase in the overall corrosion rate instead of corrosion protection. BTA was proven to be a better inhibitor on its own than when KEX is added into the solution. The increase in corrosion rate after the treatment of the coupons with BTA with KEX showed there is no synergistic effect between them in the concentrations tested.

The statistical analysis of the experiment showed that the most significant factor during all of the monitoring intervals was KEX the presence of which in the BTA solutions did not increase the inhibitive efficiency. On the contrary, the inhibitive efficiency of the mixtures of BTA with KEX resulted in accelerated corrosion. The effect of KEX is most significant in the overall experiment in all monitoring intervals. BTA is a lot less significant and becomes totally insignificant after 504 hours of exposure. Time of immersion is a lot less significant than KEX, however, the increase in the period the coupons stay immersed into the inhibitor solutions resulted in increase in weight uptake consequently decrease in inhibitive efficiency. Similar results were found in Chapter 5.
There are interactions between BTA and KEX as well as the time of immersion, throughout the monitoring period of 504 hours.

The experiments using different concentrations of BTA and KEX showed there is no synergistic effect between the two compounds. Another issue regarding these treatments was the colour alteration observed on both clean and corroded copper coupons. In the former case, the coupons lost their metallic appearance whilst in the latter the formation of

a thick dark layer changed completely the original surface of cuprite. Therefore, the experimentation with this combination did not continue as it was found unsuitable for use on archaeological objects.

6.7 BTA and KI

Potassium iodine (KI) is not an inhibitor itself, however, halide ions such as iodine can improve the adsorption of organic compounds to a metal surface. KI has been reported to improve the adsorption of BTA on copper increasing its efficiency because of the synergistic effect between them (see chapter 3). A series of three experiments were carried out to investigate if the synergistic effect

6.7.1 Experiment BTA + KI 1

The first experiment tested the combination of BTA with KI using the same concentrations used by Wu *et al* (Wu *et al*, 1993: 2792). The experiment examined the synergistic effect between BTA and KI using 0.01M concentration for each compound when applied on corroded copper. The solvent used was deionised water. The design used was a full factorial design with two factors at two levels with three replicates. The total number of coupons used was 12. The design expect of the inhibitive efficiency of the combination, allowed the evaluation of the single BTA and KI as inhibitors. The factors and their levels are shown in table 6.21.

Table 6.21. Factors and their levels examined at BTA and KI experiment 1.

Factor	Level -	Level +
BTA	No	0.01M
KI	No	0.01M

A white precipitate was formed on the copper surface immediately after immersion of the coupons into the BTA and KI solution in water.

6.7.1.1 pH

The pH of 0.01M KI was found to be 7 and increased to 9.7 after one hour of copper immersion. The pH of 0.01M BTA was 5.1 and dropped to 3.7 and to 2.8 after one and twenty four-hour of copper immersion. The pH of BTA and KI was close to that of BTA alone 5.3 and dropped after immersion to 4.3 and 4.2. The same pH values were observed for 0.1M BTA + 0.1M KI solutions.

6.7.1.2 Colour changes BTA + KI

The coupons treated with 0.1M BTA and 0.01M KI in ethanol for twenty four hours, presented a different picture. The larger part of the surface retained the metallic appearance covered with a thin layer of transparent film. On top of this film there was a patchy dark green/brown precipitant that resulted in partial loss of the metallic appearance. In other cases of the same treatment, the coupon was covered with a non-uniform layer that had a grey streak and a dark tide line in the middle.

Corroded copper coupons treated with 0.01M BTA and 0.01M KI in deionised water showed colour changes. The cuprite appearance was lost and the surface was covered with a brown/green precipitant.

6.7.1.3 Results BTA + KI 1

The results of this experiment are not easily interpreted as they change over the period of time of exposure. The coupons treated with 0.01M KI showed that although not an inhibitor it can provide some kind of protection. Two out of three coupons treated with 0.01M KI in deionised water exhibited an inhibitive efficiency of 15 and 18% after 24 hours of exposure to 95%RH. The third coupon gained a lot of weight initially and then the weight dropped dramatically showing that it provides efficiency of 22% after 48 hours of exposure. These results should be viewed with caution as the dramatic change of weight over a period of twenty four hours should be either an error during weighing of the coupon the first time, or flaking of some of the corrosion products formed on the surface therefore lower weight measurement the second time. The latter was something also observed in other cases and is considered as the most probable scenario. The coupons treated with 0.01M BTA in deionised water also exhibited deviations in the weight gained. For example, one coupon presented 70% efficiency after 24 hours of exposure which however dropped to 0% after 48 hours of exposure. Another coupon presented stable values of efficiency that varied from 25 to 27% throughout the monitoring period and the third coupon presented an efficiency of 48% after the first 24 hours of exposure that dropped to 14% after 48 hours and reached 9% after the completion of the 840 hours of exposure. The varying inhibitive efficiency shows that lower concentrations of BTA are not sufficient for the protection of corroded copper and could provide only limited protection the degree of which depends largely on the application. It is very possible to have a random human error during the application of the treatment. Table 6.23 shows the average efficiency of the treatments. Tables with all the values are given in Appendix 1.

Table 6.22. Average inhibitive efficiency values for experiment BTA + KI 1.

BTA + KI 1	Inhibitive Efficiency % (Average Values)				
Treatment	24h	48h	168h	504h	840h
BTA 0.01M/H2O	48.1	14.4	9.6	9.0	9.0
BTA 0.01M+ 0.01M KI/H2O	-21.4	-9.0	-9.8	-3.2	1.8
0.01M KI/H2O	2.8	21.7	18.1	21.7	25.0

The coupons treated with the combination of 0.01M BTA and 0.01M KI show a similar picture. Two out of three coupons gained a lot of weight resulting in accelerated corrosion of the coupons by 54 and 12% respectively whilst the third gained weight similar to the untreated coupons, providing efficiency of 2% after 24 hours of exposure. The result clearly indicated that there is no synergistic effect between the compounds when dissolved in deionised water and when used in this concentration.

The statistical analysis of the experimental outcome presents particular interest as the effect of BTA and KI change over time. The main factor affecting the inhibition process after 24 hour exposure to high RH is KI which has a negative effect on the process. Its presence in the solution resulted in increased weight uptake, thus decreased efficiency. BTA is less significant however the addition of BTA into the solutions resulted in increased efficiency. However, in the next two monitoring intervals there is a controversial outcome. KI becomes totally insignificant whilst BTA becomes the most important factor with a *negative* effect when added to the solution. At the last two intervals both factors are found to be significant for the process, with the BTA addition resulting in reduced efficiency and KI presence as positive. The two factors interact to a large extent, their interaction although significant throughout the exposure period, changes consistent with the comments for the main factors.

The concentrations used were probably too low to be effective on corroded copper and the results are not conclusive regarding the synergistic effect between BTA and KI, so more experiments followed to look more effectively into their reactions.

6.7.2 Experiment BTA +KI 2

In the second experiment concerning the combination of BTA + KI higher concentrations of the compounds were used to examine their effectiveness and suggested synergistic effect. As has been described previously, five factors were selected, however, given that there were no results for 60% RH and for clean coupons there was a similar lack of results, the experiment was subdivided to a three factor experiment to examine better factors such as the BTA and KI concentrations and their behaviour in relation to two different periods of time of immersion. From the full experiment, the most significant factors found were the RH and the copper substrate. The three factors assessed and their levels in the first full experiment and well as the one discussed here are given in tables 6.24.

Table 6.23. Levels of the factors examined in experiment 2 of BTA and KI.

Factor	Level -	Level +
BTA	0.1M	0.25M
KI	No	0.1M
Time of Immersion	1h	24h

6.7.2.1 Colour changes BTA + KI 2

The clean copper coupons, although they retained their metallic appearance, were covered with a film that had a white/grey tint. At higher concentrations (BTA 0.25M and KI 0.1M) there was also a whitish precipitate on the lower part of the coupon. Longer times of immersion resulted in the formation of a thicker semi opaque film on the surface. In the

case of 0.25M with 0.1M KI in ethanol after twenty four hours of immersion the coupon was covered with a non-uniform light green film.

Corroded coupons treated with the BTA and KI solutions presented colour changes that were dependent on the solution and the length of period of immersion. In general the greater colour changes were observed on both solutions at longer periods of immersion. More specifically, coupons treated with 0.1M BTA and 0.1M KI for an hour retained the cuprite colouration with some light green precipitate on the lower part, whilst the coupons treated with the same solution for longer (twenty four hours) were covered with a dark red/black uniform layer.

In the case of coupons treated with solutions of 0.25M BTA and 0.1M KI for an hour, there were no significant colour alterations. Nevertheless, the coupons treated with the solution for twenty four hours were covered with a non-uniform olive green film on top of which there was a grey/beige precipitate.

6.7.2.2 Results of BTA + KI 2

The results of this experiment showed that there was no synergistic effect between BTA and KI as the addition of KI into the different BTA solutions resulted in all cases in accelerated corrosion of the coupons. The most effective treatment was that of BTA 0.25M in ethanol immersed for an hour, followed by the same solution immersed for twenty four hours, then 0.1M BTA for an hour and twenty four hours in agreement with the results of chapters 5. The average values are shown in table 6.24.

Table 6.24Average inhibitive efficiency values of BTA + KI treatments of experiment 2.

BTA + KI 2	Inhibitive Efficiency % (Average Values)			
Treatment	24h	48h	168h	504h
BTA 0.1M, 1h	24.1	19.9	11.7	11.3
BTA 0.1M, 24h	19.7	14.5	10.1	3.2
BTA 0.1M + KI 0.1M, 1h	-24.6	-20.7	-18.5	-11.9
BTA 0.1M + KI 0.1M, 24h	-16.8	-12.6	-9.8	-3.8
BTA 0.25M, 1h	36.8	35.0	31.3	23.3
BTA 0.25M, 24h	32.0	26.2	20.6	8.5
BTA 0.25M + KI 0.1M, 1h	-17.3	-15.1	-13.6	31.4
BTA 0.25M + KI 0.1M, 24h	-16.3	-15.6	-9.0	-3.8

However, what is worth mentioning is that although the coupons treated with the combination of BTA + KI were not protected the weight gained remained quite stable over the period of exposure. The coupons gained initially a lot of weight, but after that the increase was a lot less than that of the other treatments where the increase of weight uptake was more substantial over time. After the 24-hour exposure to high RH there was overall corrosion of the surface of the coupons. In all coupons treated with BTA + KI flaking of a corrosion layer was observed.

6.7.3 Experiment BTA + KI 3

The addition of KI onto the copper surface could easily cause accelerated corrosion because of the presence of iodine, however there might be an optimum concentration which when added to BTA solutions could indeed improve its efficiency. The third experiment examined the BTA concentration (0.1 and 0.01M), the presence of KI (concentration used was 0.01M) and the solvent (deionised water and ethanol). All the coupons were immersed into the inhibitor solutions for twenty four hours. The total number of coupons used was 24

as each treatment had three replicates. All the treatments were applied on artificially corroded copper coupons. The factors and their levels are shown in table 6.25.

Table 6.25. Factors and the levels examined in the third experiment of BTA and KI.

Factor	Level -	Level +
BTA	0.01M	0.1M
KI	No	0.1M
Solvent	Water	Ethanol

The formation of white precipitate on the surface of the coupons observed in experiment 1 was also observed in this experiment. Interestingly, the precipitate was formed only in the aqueous solutions.

6.7.3.1 Results of BTA + KI 3

The results of this experiment were noteworthy because of the deviation they present. The treatment of 0.01M BTA in ethanol appeared to accelerate corrosion, whilst the same concentration in water seems to be effective even though the results present deviations. The results of 0.1M BTA in water and ethanol where similar to those of chapter 5, with the ethanol solution being quite effective and the aqueous solution presenting accelerated corrosion in two out of three coupons and a good efficiency (approx. 40% after 24-hour exposure) on the third coupon.

The efficiency of BTA + KI treatments varied greatly depending on the concentration and the solvent used. Interesting, whilst most of the treatments caused accelerated corrosion to the copper specimens, 0.1M BTA + 0.01M KI in deionised water appeared to be the most effective of the whole experiment with efficiency that varied from 15 to 32% after 24 hours of exposure and remained high after the completion of the 840-hour exposure with efficiency 25-31% (table 6.26). Since the treatment of corroded coupons with 0.1M BTA in

water results in accelerated corrosion when immersed into the solution for twenty four hours as it was found not only in this experiment but also in the experiments found in chapter 5, it is evident that there is synergistic effect between BTA and KI in this occasion. The efficiency increased by a significant amount, but more importantly, a totally ineffective treatment, becomes quite effective with the addition of KI.

It is also worth examining not only the inhibitive efficiency but also the weight change which in case of this treatment appears to increase less over time (smaller gradient) compared to the other treatments providing a stable inhibitive efficiency throughout. The latter is an exceptional desired result in conservation, as the effectiveness of a treatment drops significantly over time.

Table 6.26. Average inhibitive efficiency values of corroded copper coupons treated with BTA and BTA+KI of experiment BTA+KI 3.

BTA and KI, experiment 3	Inhibitive Efficiency % (Average Values)				
Treatment	24.0	48.0	168.0	504.0	840.0
BTA 0.01M/eth	-16.4	-3.9	-1.1	3.9	14.5
BTA 0.01M/H2O	47.6	26.2	21.6	15.8	21.7
BTA 0.01M + KI 0.01M/eth	-46.5	-22.9	-22.5	-7.5	-1.7
BTA 0.01M + KI 0.01M/H2O	-19.8	-2.9	-2.8	4.8	15.0
BTA 0.1M/eth	24.8	28.5	21.2	21.9	22.0
BTA 0.1M/H2O	1.3	10.6	11.9	14.9	23.4
BTA 0.1M + KI 0.01M/eth	-3.6	8.1	17.0	19.7	30.0
BTA 0.1M + KI 0.01M/H2O	23.9	30.3	30.3	31.8	37.8

Another important aspect is that this combination works only in water. Ethanol is a better solvent for BTA allowing better penetration of the inhibitor into the metal, especially when dealing with corroded surfaces but it had a negative effect in the BTA and KI treatments examined in this experiment. Two out of three coupons treated with 0.1M BTA + 0.01M KI

in ethanol gained more weight than the untreated coupons. However, one of these two coupons presented some weird behaviour as the weight dropped after 168 hours of exposure and resulted in increase of inhibitive efficiency from -3% at 24 hour-exposure to 35% after 840 hour-exposure. The third coupon had 18% inhibitive efficiency after 24 hours and 34% after 840 hours. Although the results are not always consistent there is something common in all, the inhibitive efficiency increases with time in all BTA + KI treatments, even on those that accelerated corrosion such as the treatments of equimolar solutions of 0.01M BTA + 0.01M KI in water or ethanol.

Statistical analysis of the experiment showed that all factors are significant at some point in time and insignificant at another except BTA concentration which remains the most important throughout the monitoring process with 0.1M being more effective than 0.01M. KI is the most important factor for the first 24 hours of exposure, it becomes less important over time. It's effect is, in general, negative in the overall process as its addition to BTA results in increased weight uptake with the exception of the 0.1M BTA and 0.01M KI in water discussed earlier. The solvent is also important with deionised water being more effective than ethanol. Even though the importance of each factor changes over time, their effect, positive or negative remained unvarying all the way through the monitoring.

All the factors interact, the type of interaction and its importance also changes over time. However the most important interaction is that of BTA with KI followed by the interaction between BTA and solvent and after 504 hours of exposure, there is interaction even between KI and the solvent.

The combination of BTA + KI was proven to be quite variable depending to a large extent on the concentration and the solvent used. These results proved that there is possible synergism between BTA and KI and their combination could be successful if used properly. However, the parameters and the effect of each factor should be further examined and defined. The addition of halide on a metal surface was expected to be potentially risky, yet promising. The analysis of the treated coupons that follows in this chapter explain better the reactions taking place between copper and KI as well as copper, BTA and KI.

6.8 BTA and PMT ($C_7H_6N_4S$)

6.8.1 Experiment BTA + PMT 1

The first experiment examined the possible synergism of BTA + PMT by using the concentrations already tested. The same concentration (0.005M) was used for both compounds. The factors tested were BTA and PMT. The coupons stayed immersed in the solutions for thirty minutes as recommended in the literature. The solvent used was deionised water. All of the treatments were applied on artificially corroded coupons and were placed into the environmental chamber at 95±5%RH and 25±1°C. The total number of coupons used for this experiment was 12. Table 6.27 shows the factors tested and their levels. The design allowed the direct comparison of the combination of BTA + PMT with BTA and PMT alone.

Table 6.27. The factors examined in the first of BTA and PMT and their levels.

Factor	Level -	Level +
BTA	No	0.005M
PMT	No	0.005M

All the solutions were clear. However, the coupons immersed in the 0.005M solution of PMT in water were covered within five minutes with grey sediment.

6.8.1.1 Colour alterations BTA + PMT 1

The clean coupons did not present any significant changes in their metallic appearance in all treatments (see Fig 6.4). The corroded coupons treated with 0.005M BTA in deionised water exhibited a light green colouration although the colour of cuprite was largely retained. Similarly, coupons treated with 0.005M PMT in deionised water presented in part a yellow/green surface colouration. An interesting note is that the coupons while in solution were covered with a light grey precipitate which, because of its weak consistency was dissolved from the coupon during its removal from the solution. Coupons treated with the mixture of BTA and PMT were covered with a yellow/green film that was detached during their removal from the solutions.

6.8.1.2 Results BTA + PMT 1

All coupons treated with the three treatments (BTA, PMT and BTA + PMT) showed similar weight changes. Therefore, all the tested treatments exhibited inhibitive efficiency values very close to each other. After twenty four hours of exposure, the efficiency of 0.005M BTA was between 23 and 37%, of 0.005M PMT was between 12 and 37% and the 0.005M BTA + 0.005M PMT solution provided protection of 26 and 47% (average values in table 6.28). These values showed that the combination of BTA with PMT was only slightly more effective than the BTA or PMT on their own. It is possible to have some synergism between the inhibitors even if the efficiency was not increased dramatically. In

general, the increase of the BTA efficiency when PMT was added was not sufficient to draw conclusions as to whether there was a synergistic effect or not between the compounds.

Table 6.28. Average inhibitive efficiency values of BTA + PMT 1 treatments.

BTA + PMT 1	Inhibitive Efficiency % (Average Values)				
Treatment	24h	48h	168h	504h	840h
0.005M BTA/H2O	30.2	30.3	30.2	28.2	21.0
0.005M BTA + 0.005M PMT/H2O	34.3	31.0	29.2	24.9	23.0
0.005M PMT	22.0	32.1	25.8	37.8	35.5

The analysis of the experiment showed that both factors were significant for the process and their presence had a positive effect on the overall process. The significance of the factors changed over time. In general both factors were significant with BTA being more significant at the beginning and PMT being more important factor at the end of the monitoring process (504 and 840 hours of exposure). There was also clear interaction between the two factors with a positive effect.

The analysis of the experiments also showed the sequence of importance between main factors and interactions. That is, that after 24 hours of exposure to 95±5% RH, interaction of BTA and PMT was most important followed by PMT, and after 48 hours, the effect is reversed with PMT being more important than the interaction of BTA with PMT followed by BTA. After 168 hours, BTA became more important, followed by the interaction of BTA with PMT and then PMT alone. At 504 hours PMT became more significant followed by the interaction of BTA with PMT and finally after 840 hours of exposure, PMT was the most significant followed by the interaction of the two compounds. These results not only

confirm the existence of interaction between BTA and PMT but also demonstrate the positive effect this interaction caused to the overall process.

6.8.2 Experiment BTA + PMT 2

The second experiment examined the five factors as described at the introduction of this section, including the BTA concentration, the presence of PMT, the time of immersion, the RH and the substrate. The solvent used in all treatments was ethanol, analar grade. The RH and the substrate were the most important factors. In order to assess the other three factors, the experiment was subdivided into a three factor experiment assessing the BTA concentration (0.1M and 0.25M), the PMT presence and the time of immersion. The factors and their levels are shown in table 6.29. The original number of coupons treated in the five factor experiment was 96, the number of coupons used and discussed in this experiment was 24. Each treatment had three replicates.

Table 6.29. The second experiment of BTA + PMT examined BTA concentrations in relation to PMT and the time of immersion.

Factor	Level -	Level +
BTA concentration	0.1M	0.25M
PMT	No	0.1M
Time of immersion	1h	24h

6.8.2.1 Colour alterations BTA + PMT 2

No colour changes were observed on clean copper coupons treated with the BTA + PMT solutions. The coupons kept their metallic appearance. The film on the surface was not always uniform, with some whitish tidelines found on the surface of some coupons because of drying. The time of immersion did not seem to affect the appearance of the coupons, as

the coupons kept their metallic appearance in all treatments. In case of coupons treated with 0.25M BTA + 0.1M PMT the tide lines were a little more pronounced than in the other treatments.

Corroded coupons treated with the mixture of BTA + PMT appeared slightly darker. In general the colour of cuprite was retained with some darker areas, making the surface colouration non-uniform. In the case of coupons treated with 0.1M BTA + 0.1M PMT for an hour, there were minimum colour changes. After twenty four hours, the coupons appeared darker although they still retained the cuprite appearance. Coupons treated with 0.25M BTA + 0.1M PMT for an hour did not present great colour alteration. The cuprite layer was retained with some darker areas. However, coupons treated with the latter solution for twenty four hours were covered with a dark brown layer. As a conclusion, longer periods of immersion caused a darkening of the surface whilst the concentration of the solution had a smaller effect on the changing appearance of the coupons.

6.8.2.2 Results of BTA + PMT 2

The most effective treatments were those of 0.25M BTA in ethanol followed by 0.1M BTA in ethanol. The treatments using the combination of BTA + PMT did not show greater inhibitive efficiency than BTA on its own. An exception to this was the treatment of 0.1M BTA + 0.1M PMT when the coupons stayed immersed for an hour into the solution. Two out of three coupons exhibited a satisfactory result with inhibitive efficiency 26-27% after 24 hours, 21-23% after 48 hours and 12-14% after 168 hours which dropped dramatically to -6% after 504 hours of exposure (see table 6.30). The third coupon showed accelerated

corrosion from the beginning of exposure. The other solutions of the combination also showed similar results. Up to 168 hours of monitoring, there was some effectiveness which however dropped at 504 hours to negative values.

The analysis of the experiment showed that the most important factor throughout the monitoring of the process was the presence of PMT. Compared to the effect of PMT, the BTA concentration had a small effect (with 0.25M being more effective) as well as the time of immersion (with one hour being more effective than twenty four hours of immersion). However, its presence had a negative not a positive effect. There was clear interaction between BTA + PMT for 168 hours of exposure but no interaction at 504 hours.

Table 6.30. Average values of inhibitive efficiency of BTA + PMT 2.

BTA + PMT 2	Inhibitive Efficiency % (Average Values)			
Treatment	24h	48h	168h	504h
BTA 0.1M, 1h	24.1	19.9	11.7	11.3
BTA 0.1M, 24h	19.7	14.5	10.1	3.2
BTA 0.1M + PMT 0.1M, 1h	15.0	13.0	6.8	-6.9
BTA 0.1M + PMT 0.1M, 24h	6.3	5.2	1.2	-10.0
BTA 0.25M, 1h	36.8	35.0	31.3	23.3
BTA 0.25M, 24h	32.0	26.2	20.6	8.5
BTA 0.25M + PMT 0.1M, 1h	11.3	8.0	4.8	-6.6
BTA 0.25M + PMT 0.1M, 24h	9.8	8.4	5.3	-4.5

This is not the first time that a combination of inhibitors showed synergistic effect between two compounds dependent on the concentrations used. In this experiment there was no evidence of a synergistic effect when more concentrated solutions were used. The combination of BTA with PMT appeared promising, however, more experiments are

necessary to define the optimum range of concentration for it to be more effective than BTA alone.

6.8.3 Comparative study of factors affecting combinations of inhibitors

The experiments carried out on all six combinations of BTA with the selective compounds showed a variety of trends. One of the first observations was related to the effectiveness of these compounds. BTA + AMT presented a very strong synergistic effect that was observed in all solutions tested. BTA + BZA caused acceleration of corrosion, as did BTA + ETH. The testing of BTA + KEX also proved to be ineffective, whilst the combination of BTA + KI although a failure accelerating corrosion in the majority of tested treatments showed there is possibly some synergism with BTA in one particular solution mixture that might be relevant for archaeological copper and copper alloys. Finally, the combination of BTA + PMT although it appeared to be less effective than BTA or PMT when used alone, did not cause acceleration of corrosion.

The behaviour of these combinations on the different factors examined presented interesting data as to the significance of the concentration, the time of immersion or the solvent change depending on the compounds tested. In chapter 5 it was found that the BTA is affected foremost by the time of immersion, with longer immersion resulting in decrease of effectiveness of a treatment. The concentration was also important, although having less of a dramatic effect on the efficiency as the duration of immersion. The solvent selection also affected the process but it was more its interaction with the time of immersion that was the cause of this. For example, although corroded coupons treated with 0.1M BTA in water

immersed for an hour could be satisfactorily protected, the same treatment at longer periods of immersion could result in acceleration of corrosion (see Chapter 5).

The treatment of BTA + AMT showed that because of the synergistic effect between the compounds, the other factors examined (solvent, time of immersion, etc.) were almost insignificant. The solution was effective in all concentrations used, all solvents and both periods of immersed tested. This clearly demonstrates that the synergism between these compounds is stronger than any other factor that could possibly affect the process.
In the experiments with BTA and BZA it was clear that although the efficiency of BTA is affected and governed by the same factors as in chapter 5, the combination of the compounds was ineffective in all different concentrations, solvents and periods of immersion.

6.8.4 pH of solutions

Table 6.31 summarises selected pH measurements of the compounds tested. BTA and AMT are mildly acidic, whilst KI, ETH and BZA are neutral or alkaline. The pH in most solutions decreased after immersion of corroded coupons due to their reaction with copper. The difference was more obvious when corroded coupons were immersed. The pH of aqueous 0.1M BTA solution dropped from 5.8 to 4.2 after one hour and to 3.6 after twenty four hours of immersion of corroded copper. Similarly, the pH of aqueous 0.01M AMT which is 4 decreased to 3.3 and 2.7 after one and twenty four hour immersion of corroded copper respectively.

The combination of BTA + AMT has low pH which however does not present any significant pH change after immersion of copper. This might be due to immediate reaction between the inhibitors and the copper. The almost unvarying pH values of the solution might be another indication of the synergistic effect between the two compounds.

Table 6.31. pH values of aqueous inhibitor solutions before and after immersion of corroded copper coupons.

Aqueous Solutions	pH		
	Before coupon immersion	after 1h of coupon immersion	after 24 hrs of coupon immersion
BTA 0.1M, pure	5.8-5.5	4.1-4.2	3.5-3.6
BTA 0.01M	5-5.1	3.6-3.7	2.75-2.8
BTA 0.1M + AMT 0.01M	4.1-4.2	4.1-4.2	3.9-4
AMT 0.01M	4	3.3	2.7
BTA 0.1M + ETH 0.1M	9.6	9.6	9.5-9.6
ETH 0.1M	11	10.7	10.6
ETH, (1.8 ppm)	9.5	9.5	9.4
BTA 0.1M + KI	5.3	4.3	4.2
KI 0.01M	7.0	9.7	
BTA 0.1 + BZA 0.1	8.1	8.1	8
BZA 0.1	10.8	10.2	10
BTA + KEX	7.4	7.4	7.4

The aqueous KI solution has neutral pH, however the combination of BTA + KI solutions resulted in lower value than 0.1M BTA alone which decreased with immersion of the copper coupon. The combination of BTA + KEX resulted in neutral pH which remained constant even after immersion of copper. The same phenomenon of constant pH value was observed in the solutions of BTA + BZA and BTA + ETH which was mild alkaline solutions.

It is worth mentioning that Metikoš-Huković *et al* (2000: 617-624) reported the importance of the pH for the adsorption of BTA on copper. At alkaline conditions the reaction was found to be instant due to the complete dissociation of BTAH to BTA^- whilst at neutral and slightly acidic pH values the Cu-BTA film was found to be time dependent. Still BTA was found to be effective in a pH range 4-10. The results of the accelerated corrosion tests are directly linked to the pH values.

6.8.5 Weight change of coupons after treatment

The weight of the coupons after the inhibition treatments varied depending on the treatment, the concentration and the application methodology. It is known that the films formed are usually very thin and in some cases not visible. However, as was discussed earlier, in some cases the treatments resulted in major surface alterations, also remarkable through the weighing of the coupons before and after the inhibition treatment. Some of the treatments caused little if any changes, others resulted in weight uptake and there were few examples that resulted in weight loss. This weight might be indicative of the reactions between the inhibitive compounds and film formation.

The amount of weight gained from BTA treatments depends primarily on the solvent and secondly on the concentration. Corroded coupons treated with 0.01M in both solvents and 0.1M in water gained 0.01% of their weight whilst coupons treated with 0.1M BTA gained around 0.05% of their weight. Although coupons treated with 0.01M AMT lost weight (-0.08%) the BTA + AMT combination resulted in minor weight gain, 0.01-0.02%. Treatments of BZA, BTA + BZA resulted also in small weight gain, whilst ETH, BTA +

ETH, PMT, BTA + PMT treatments exhibited weight loss after the treatment (0.4-0.6% of their weight was lost).

Coupons treated with BTA + KI solutions showed a varied weight change. For example, the treatment of 0.1M BTA + 0.01M KI on both solvents used, resulted on inconsistent weight gain and/or loss. Some of the coupons gained and some lost weight. Those treated with 0.01M BTA + 0.01M KI gained 0.18% on average of their weight. Coupons treated with KEX lost weight, however, those treated with BTA + KEX gained a small amount. The increase in concentration resulted in more weight uptake.

The weight changes after the inhibition treatments although small could be linked to the way these compounds are bonded to copper and whether the complex formed on the surface is the result of a dissolution-precipitation mechanism or not. Once more it was clear that concentration, solvent and the time of immersion affected the result. Weight loss does not necessarily imply dissolution-precipitation mechanism as the mechanism could result in weight gain due to a thicker precipitation of the film. In chemisorbed films the weight should changes should be minor. To assess better this aspect, measurements on a micro level is found necessary (e.g. microbalance).

6.8.6 Behaviour of treated corroded coupons to high RH

Of great interest is the way clean and corroded coupons treated with different inhibitors/combinations of inhibitors react to high RH. Some of them present signs of pitting corrosion, whilst in others there is the flaking of a corroded layer. The way

corrosion evolves can answer some questions regarding the film formation, its adherence on the copper substrate and its efficacy. Factors such as the concentration of the solution, the period of time of immersion and the solvent affect the efficiency of the inhibitor and consequently the way the coupons corrode. These points refer to inspections carried out on all the groups of treated coupons after their twenty-four hour exposure to 95±5% and 25±1°C.

Untreated controlled coupons corrode under the same conditions. There is a layer of active corrosion which is formed on the surface which is flaking and underneath this there is also well developed pitting corrosion. Naturally, corrosion is more developed on the edges due to the edge effect discussed in chapter 4. The surface of the coupons that does not present pitting corrosion exhibits the colour of cuprite, which in some cases appears darker and or more reddish than the original surface.

Coupons treated with BTA solutions showed that the film is well adherent on the copper substrate even as the corrosion develops on other parts of the surface in the form of localised and uneven corrosion. The observation of coupons that have been treated with BTA under the SEM confirmed these observations. The corrosion pit develops as a sphere (due to a defect in the film causing a point of failure) which lifts the inhibitor film (see photo 5.9 of chapter 5).

The coupons treated with BTA + AMT presented a similar picture to that of BTA, however, since these solutions were more effective than BTA alone, the extent of corrosion was more restricted as pitting corrosion.

The combination of BTA + BZA was not found to be effective for copper. This result is also illustrated by the fact that the surface is covered with a corroded flaking layer, beneath which there is also pitting corrosion.

A similar picture can be observed commonly on coupons treated with BTA + ETH. There was formation of a flaking corrosion layer. The film was less flaky than that of BZA and in case of 0.25M BTA + 0.1M ETH immersed for twenty four hours, the film was only partly flaking whilst in some parts it appeared well adherent on the substrate with pitting corrosion developing on its surface.

It is worth mentioning that corroded coupons treated with ETH did not present corrosion after the exposure as most of the corrosion layer was dissolved into the solution leaving behind a partly "cleaned" or corrosion free porous surface due to surface etching.

A similar situation to that of BTA + BZA and BTA + ETH solutions was that of BTA + KEX. After exposure to high RH, the formation of a flaking green corroded layer could be observed. The difference with the other solutions was that the film appeared thicker in an SEM image in case of more concentrated solutions (e.g. 0.25M BTA + 0.1M KEX) which

resulted in total detachment of the layer from the substrate. In the case of 0.1M BTA + 0.1M KEX the film although still flaky was partly adherent on the copper substrate.

The combination BTA + KI appeared to accelerate corrosion in most solutions tested with the exception of 0.1M BTA + 0.01M KI in deionised water. There was the formation of a thick corrosion layer which flaked off. Coupons treated with more concentrated BTA + KI solutions (e.g. 0.25M BTA + 0.1M KI in ethanol) appeared as a thick flaking layer underneath of which there was clear evidence of pitting corrosion.

Coupons treated with BTA + PMT appeared partly adherent on the substrate and partly flaky. The more adherent films were those treated with 0.1M BTA + 0.1M PMT in ethanol where the film was only partly flaking. In case of one hour of immersion the coupons presented mainly pitting corrosion and only part flaking of the film.

6.8.7 Observations on weight changes of treated clean copper coupons

It is interesting to note that out of the clean copper coupons treated with different combinations, some gained weight after the exposure in high RH. More specifically, coupons treated with 0.1M KI gained 0.004-0.0013 g after the 840 hour-exposure to high RH. The average value was 0.0008 g which was more than the untreated copper coupons (maximum weight 0.0011) that gained 0.0005 g. This shows that the immersion into KI solution could have resulted in an increase of corrosion. From the other treatments only those treated with KEX gained some weight (average value 0.0006 g) whilst the rest did not present any significant weight changes.

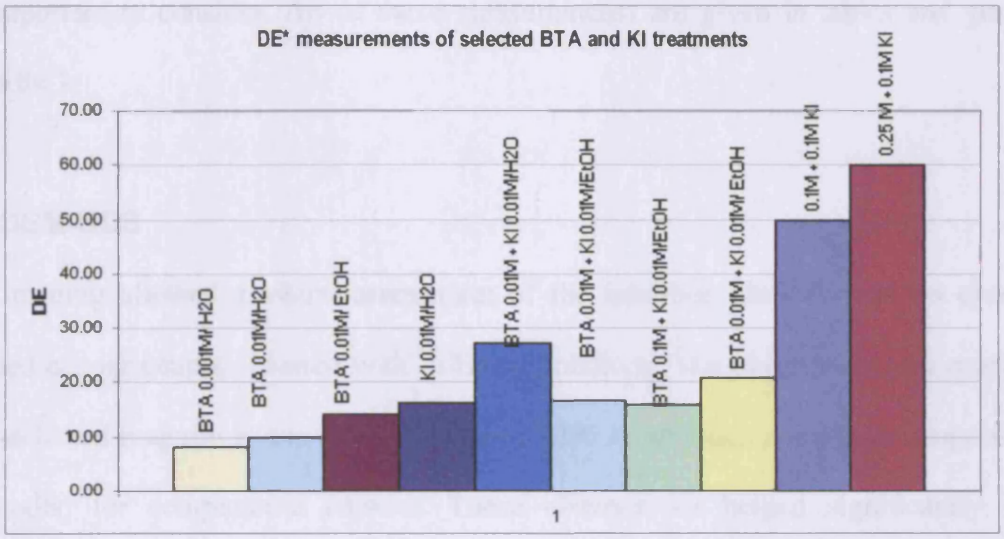
6.8.8 Comparative colour changes on clean coupons

All of the combinations tested altered to a certain degree the surface colouration. The treatments that caused the greater changes were those of BTA + KEX followed by the treatments of BTA + KI. The treatment of coupons with BTA + ETH and BTA + BZA also caused colour changes. The combinations of BTA + PMT and BTA + AMT were those that caused the least colour changes. The colour alteration of BTA solutions alone was actually greater than those of the combination treatments.

6.9 Colour measurements of treated coupons

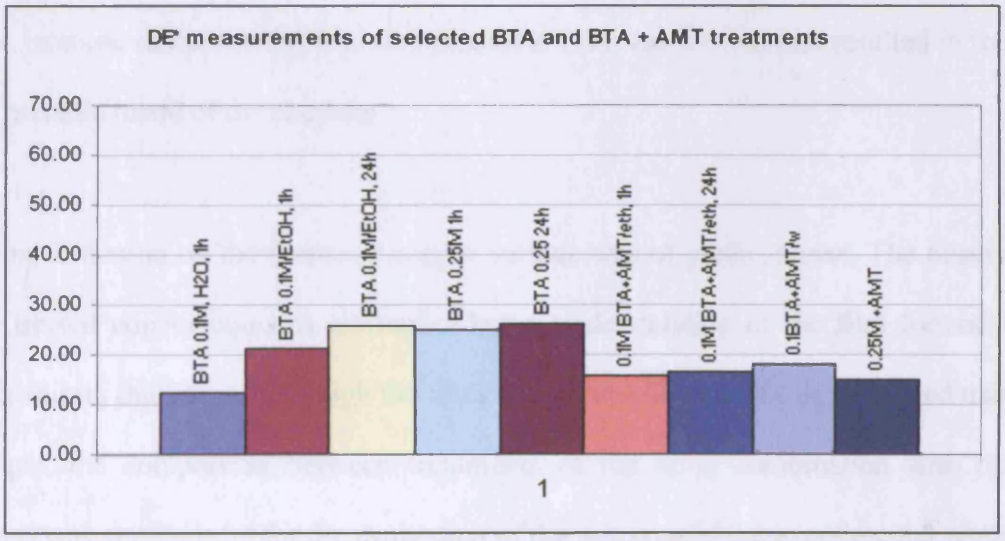
Colour perception is often a subjective matter hence colour measurements using a chromameter were employed to demonstrate colour changes instigated on corroded copper by the tested inhibitors (see chapter 4). ΔE^* is the difference in colour, chroma, hue and lightness between a treated coupon and an untreated reference coupon. The calculated ΔE^* allows an immediate comprehension of these changes as, the higher the ΔE^* is the greater the change in colour. The ΔE^* values of tested treatments are given in Appendix 2. From these values one can confirm that variables of little or no significance for the efficiency of a treatment still affect the appearance of the coupons by causing colour changes. Graphs 6.1 and 6.2 show the way ΔE^* changes depending on the solution used to treat corroded copper coupons. The values presented here are average values of three measurements taken.

The ΔE^* values in the case of BTA + KI treatments showed that the treatment with the greater colour change is that of 0.25M + 0.1m KI 0.1M followed by BTA + 0.1M KI dissolved in ethanol.



Graph 6-1. Average DE* values of BTA, KI and BTA + KI treatments on corroded copper coupons.

The comparison of the BTA and BTA + AMT ΔE* values shows that the addition of AMT into the BTA solution reduces the colour alterations in all but the aqueous solution.



Graph 6-2. DE* values showing the colour changes of BTA+ AMT treatments.

Often, colour alteration, therefore ΔE* values of different areas of the same coupon can be different. Another important issue to discuss is that in some cases ΔL*, Δa* and Δb* are

also important to consider. All of these measurements are given in tables and graphs in Appendix 3.

6.10 SEM-EDS

SEM imaging allowed a visual assessment of the inhibitor films formed on clean and corroded copper coupons treated with different solutions. The observation was carried out in pre-selected magnifications (400, 1000, and 4000 in all cases and higher magnification for details) for comparative reasons. These observations helped significantly in the understanding of the different combinations and the protection they provide to the metal. Untreated copper coupons and coupons treated with single compounds were also examined for comparison.

Although the majority of the treatments did not cause any visual difference on clean copper, in some cases like KEX a thick insoluble film was formed that resulted in total loss of the metallic lustre of the coupons.

The film formation on the corroded copper surface was of great interest. The observations of the treated copper coupons allowed a better understanding of the film formed on the surface and its thickness. Although the thickness of the film cannot be measured using this technique, the comparison between treatments of the same combination with different solutions was very helpful for the evaluation of the outcome of the experimental work.

In general, it was found that the lower the BTA concentration, the less altered the copper surface was found to be. In addition, the time of immersion also affected the surface condition. All the factors that were found to affect the inhibitive efficiency of BTA were

noticeable under the SEM.

The observation of BTA treated surfaces, under SEM are found in chapter 5. The SEM observations are discussed according to combinations. All of the data collected during the analysis are found in Appendix 4.

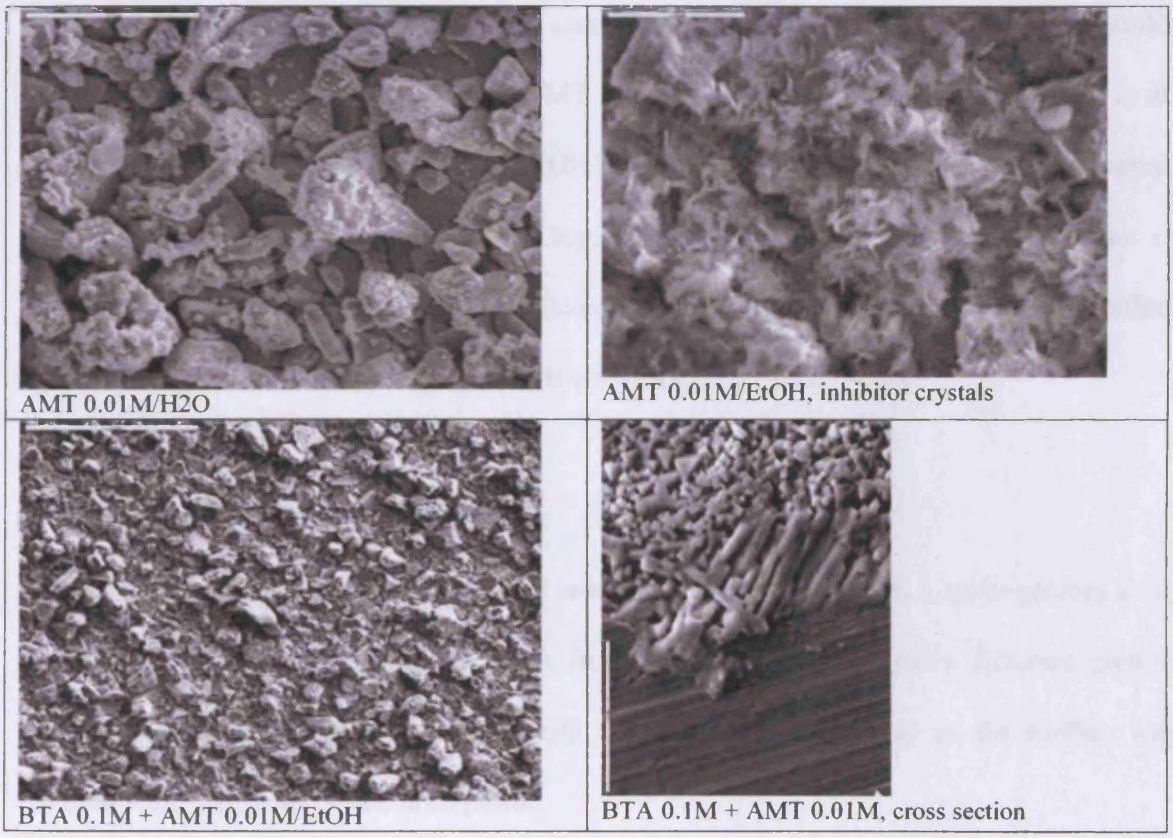


Figure 6-5. SEM image of 0.01M AMT on corroded copper.

Figure 6-6. AMT crystals formed on corroded copper after treatment with 0.01M AMT/EtOH.

Figure 6-7. Corroded copper treated with 0.1M BTA + 0.01M AMT/EtOH presents similar image to that of untreated copper.

Figure 6-8. Cross section of corroded copper treated with 0.1M BTA+ 0.01M AMT/EtOH.

6.10.1 SEM imaging of BTA + AMT

Clean copper coupons treated with AMT presented a uniform film formation. Corroded copper coupons treated with 0.01M AMT in both solvents tested (i.e. deionised water and ethanol) showed that the film formed was quite thin, following the copper oxide crystals of

the surface (Fig. 6.5). In case of AMT in water, there was some precipitate on the surface, probably tide line because of drying. When AMT was dissolved in ethanol the surface presented the formation of a continuous film on top of which there was formation of small inhibitor crystals.

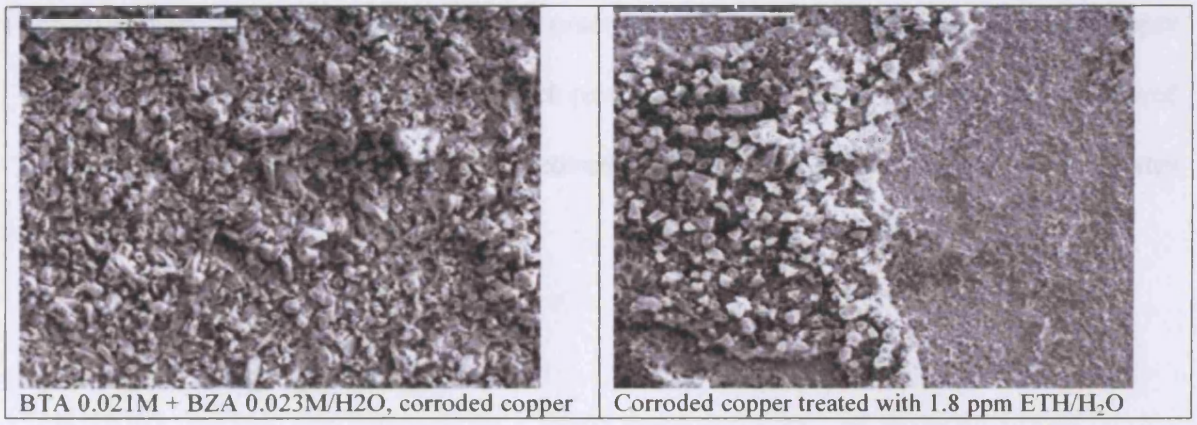
Corroded coupons treated with different combinations of BTA + AMT showed a similar picture to that of coupons treated with AMT alone. The cuprite crystals were visible in all cases (BTA concentration varied from 0.01M-0.25M and AMT was 0.01M) with small (possibly inhibitor) crystals formed on top. It seems the concentration or the time of immersion did not affect the film formed, unlike BTA where these factors affect significantly the film with precipitates on the surface (Figures 6.6-6.8).

6.10.2 SEM imaging of BTA + BZA

Whereas clean copper treated with BZA seemed to be covered with a homogenous film, corroded copper treated with 0.1M BZA in ethanol presented a totally different picture from that of untreated copper. The cuprite crystals were not visible as the surface was covered with island-like thick precipitate.

Clean coupons treated with BTA and BZA were covered with a uniform film. However, despite appearing uniform, there were micro cracks. Interestingly, coupons treated with 0.25M BTA + 0.1M BZA in ethanol presented more cracks than coupons treated with lower concentration solutions (i.e. 0.1M BTA and 0.1M BZA in ethanol).

Corroded coupons treated with 0.25M BTA + 0.1M BZA showed a very clear picture of the cuprite crystals covered with a uniform film. The coupons treated with the other solutions presented a slightly different picture where the coupons treated with 0.1M BTA + 0.1M BZA in water have well defined copper crystals covered with film whilst those treated with the same solution in ethanol had a more "fluffy" appearance with the cuprite crystals less visible. In all cases the smaller cubic crystals visible on corroded copper were not visible any more. Figure 6.9 shows the surface of corroded copper treated with BTA + BZA.



BTA 0.021M + BZA 0.023M/H2O, corroded copper

Corroded copper treated with 1.8 ppm ETH/H_2O

Figure 6-9. Corroded copper treated with 0.021M BTA + 0.023M BZA /H2O.

Figure 6-10. ETH treatment partly etched the surface of corroded copper. Two distinct phases can be seen with SEM. The area on the right part of the image is etched.

6.10.3 SEM imaging of BTA + ETH

Clean coupons treated with ETH solutions were covered with a homogeneous film. However, corroded coupons present a very different picture than that of the untreated ones. There were distinct areas on the copper surfaces, one of which has most of the corrosion layer dissolved and covered with a film similar to that of clean copper, although slightly thicker and less smooth. The other area was still covered with corrosion products which were covered with heterogeneous film. This SEM observation can explain the results of the first experiment where these coupons lost significant amount of weight. It seems that ETH

dissolved a large part of the corrosion products, visible even macroscopically (see SEM image in Fig. 6.10).

Clean coupons treated with BTA + ETH solutions were covered with a uniform not very smooth film with microcracks throughout. Corroded coupons treated with 0.1M BTA + 0.1M ETH in water were covered with an uneven film. The film covered the cuprite crystals however there were also precipitates. The same solution dissolved in ethanol appeared very similar to the picture of untreated copper with very well defined copper crystals. More concentrated solutions such as 0.25M BTA + 0.1M ETH in ethanol showed a slightly thicker film formation which covered the copper crystals and some precipitates on top.

6.10.4 SEM imaging of BTA + KEX

Clean coupons treated with KEX solutions displayed a completely different picture than that of the other treatments examined up to now. The coupons were covered with a thick heterogeneous film with needle-like three-dimensional structures that obscured the metallic surface. The treatment of corroded coupons with KEX solutions resulted in loss of the crystal definition of the cuprite crystals. The cuprite crystals were covered with round structures with three-dimensional needle-like crystals of the inhibitor.

Clean coupons treated with 0.1M BTA + 0.1M KEX were covered with a heterogeneous layer where the background had domed structures of the inhibitor on top of which there were a series of larger structures resembling flowers made of clusters of petal-like

elements. More concentrated solutions (0.25M + 0.1M KEX) also showed a heterogeneous film. The surface was covered with three layers, the first two quite similar to those described earlier except that the first layer (the one attached to the metal core) was hardly visible since the second layer (petal-like round structures) covered most of it. The difference is that there are three-dimensional round structures on (Figures 6.11-6.14).

The situation observed on corroded coupons treated with BTA + KEX was different, depending more on the solvent and less on the concentration of the solution. Thus, coupons treated with 0.1M BTA + 0.1M KEX showed the formation of a three-dimensional porous film with shaft-like open structures covering the copper crystals. The equimolar solution dissolved in ethanol resulted in a totally different picture where the surface was covered with smaller round structures that cover the cuprite crystals. There were also precipitates found sporadically over the surface. Coupons treated with 0.25M BTA + 0.1M KEX presented a similar picture to the latter, however the crystals were larger and there was a more distinctive formation of three-dimensional needle-like structures. There were also flower-like formations similar to those observed on coupons treated with KEX alone.

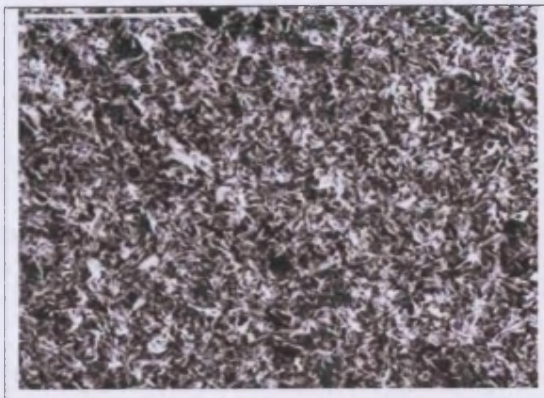


Figure 6-11 Clean copper treated with 0.1M KEX/H_2O is totally covered with three dimensional structures.

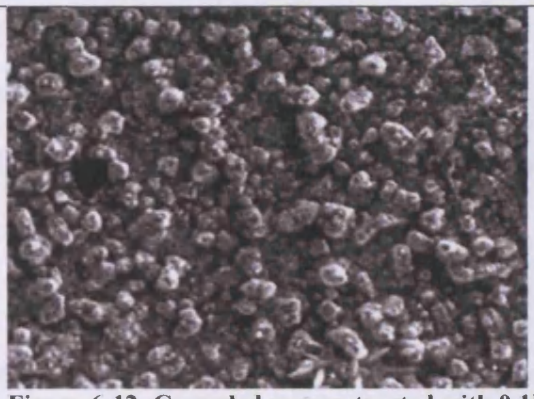


Figure 6-12. Corroded copper treated with 0.1M KEX/H_2O is covered with round "structures". The cuprite crystals are not visible anymore.

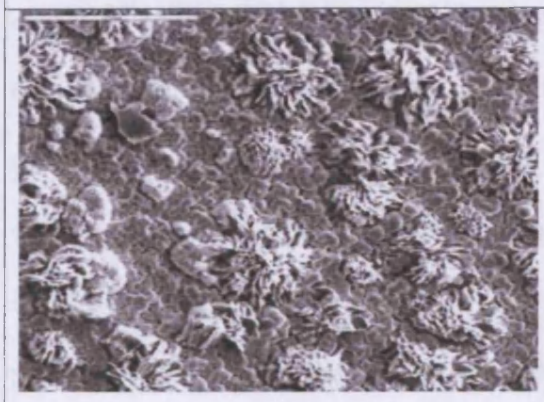


Figure 6-13 Clean copper treated with 0.1M BTA + 0.1M KEX/H2O also covered the metal with an heterogeneous film.

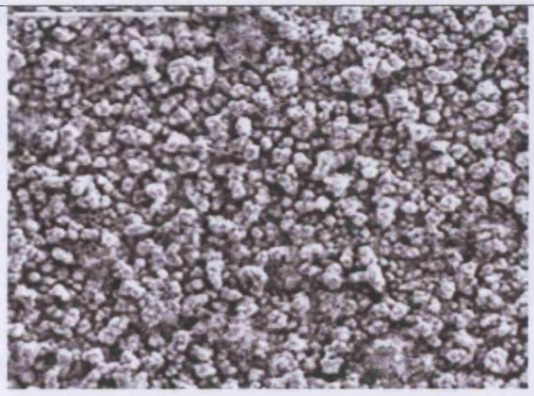


Figure 6-14. Corroded treated with 0.25M BTA + 0.1M KEX/EtOH presents also three-dimensional structures, similar to that of fig. 6.8.

In general, all of the coupons treated with KEX or BTA + KEX were covered with thick, three-dimensional films that hid the cuprite crystals. The solvent, and to a lesser extent, the concentration, affect greatly the film formed on a microscopic level.

6.10.5 SEM imaging of BTA + KI

KI is not an inhibitor in itself and this was confirmed microscopically as clean copper immersed in KI solutions was not covered with a film but with small KI crystals. Corroded coupons treated with 0.01M KI in water were covered with a thick porous film that did not

appear to be well coherent to the surface (Fig. 6.15). Coupons treated with 0.1M KI in water were covered with a heterogeneous layer of KI with a three-dimensional film that at high magnification showed a clear KI crystal formation. In all cases the cuprite formation was lost.

In all cases of clean copper coupons treated with the combination of BTA + KI there was a uniform layer presumably of BTA, with very distinctive white KI crystals in dendritic form on top. The film formed on corroded coupons depended on the solution. Thus, coupons treated with 0.01M BTA + 0.01M BTA in water presented an image similar to that observed on coupons treated with 0.01M BTA in water, with some darker precipitate on some areas and clear definition of the copper crystals. The surface of coupons treated with 0.1M BTA + 0.1M KI in water was similar to that observed previously with more whitish precipitates that cover the cuprite crystals. Finally, coupons treated with 0.25M BTA + 0.1M KI in ethanol showed a completely different arrangement (Fig. 6.16). The cuprite crystals were totally covered with a heterogeneous three-dimensional layer which coated the cuprite crystals. There were two distinctive phases, the first a complicated beehive-like porous structure and on top of this spheres formed of needle-like crystals and other crystals of different dimensions and shape.

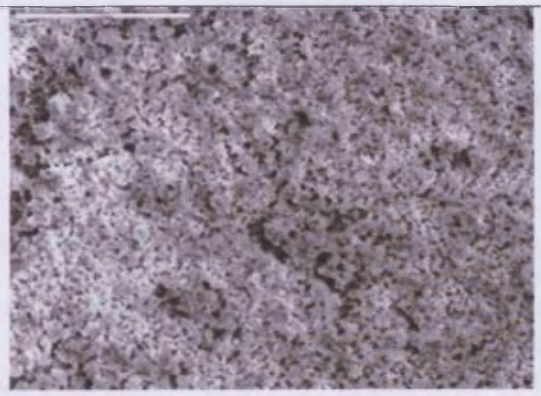


Figure 6-15. Corroded copper treated with 0.01M KI/H_2O.

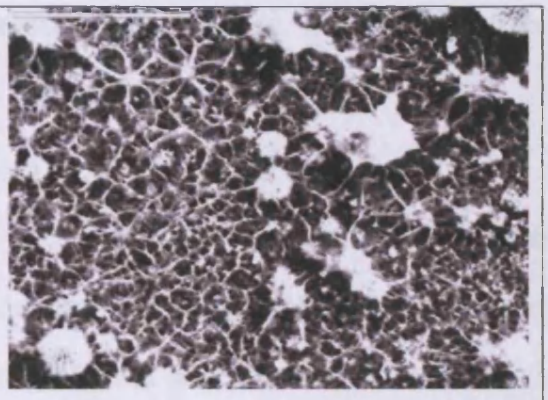


Figure 6-16. Corroded copper treated with 0.25M BTA + 0.1M KI.

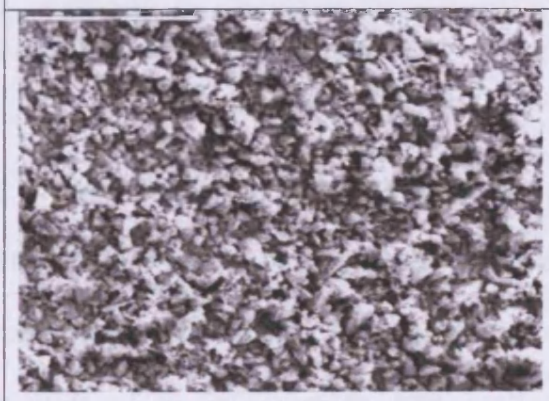


Figure 6-17. Corroded copper treated with 0.005M PMT/EtOH.

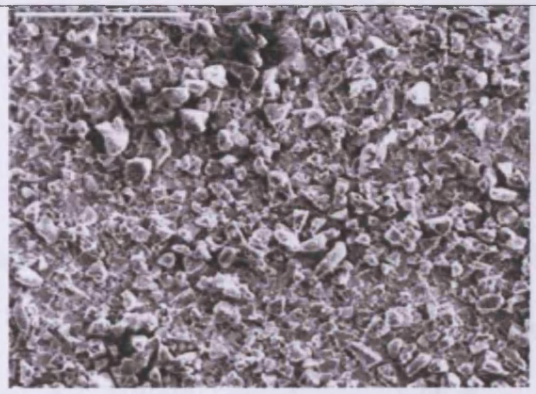


Figure 6-18. Corroded copper coupon treated with 0.1M BTA + 0.1M PMT/EtOH.

6.10.6 SEM imaging of BTA + PMT

Clean coupons treated with 0.005M or 0.1M PMT in water were covered with a uniform layer with some small holes. In case of 0.1M the film also showed cracks throughout. Corroded coupons treated with 0.005M in water appeared similar to untreated coupons with very well defined cuprite crystals whilst those treated with the same concentration in ethanol is presented a different picture. The surfaces were covered with a film following the surface with slightly reduced definition of the cuprite crystals and widely spread precipitates (Fig. 6.17). Coupons treated with 0.1M PMT in ethanol presented a similar picture with less precipitates. In case of 0.1M in ethanol the film formed followed the

surface details to a lesser extent with small crystals formed on top. It appeared that the solvent affected the film formation significantly on a microscopic level.

Clean coupons treated with the combination of BTA + PMT were covered with a uniform layer with occasional small holes. The corroded coupons of all BTA + PMT solutions appear very similar to the untreated ones with thin films and very well defined cuprite crystal surface details (6.18). The concentration and/or the solvent did not appear to affect the film formation in this case.

6.11 FTIR analysis of combinations

The FTIR analysis examined the bond changes occurring during the reaction of the compounds with copper. Each compound was analysed on its own, followed by selected analysis of treated coupons with each compound initially on its own and then in combination with BTA. The samples were placed in a holder and were analysed using absorption reflectance FTIR spectroscopy. The main functional groups and their IR bands of each compound were used for the interpretation of the results.

The interpretation of FTIR spectra when dealing with combinations of inhibitors is often difficult as shifting of peaks can lead to wrong assumptions. The assignment of peaks was carried out taking into account the general trends observed in the spectra, comparison of the spectra with reference spectra of pure compounds as well as spectra of single inhibitors with copper. The presence of a complex is confirmed by more than one peak therefore, all the peaks, their intensities, possible shifts and their relation to other peaks were taken into

account for the interpretation. Reference textbooks on spectral identification and relevant papers were also used for the interpretation (Smith, 1998, Burns and Ciurzak, 2001 and online sources-Mattson Instruments).

6.11.1 BTA + AMT $C_2H_3N_3S_2$

The reference spectrum of AMT is characterised by four thioamide bands (I-IV) as well as the stretching of NH bond. AMT is most probably bonded to copper through the deprotonated nitrogen and sulphur of the thioamide group. According to Zucchi *et al* (1998: 1927-1937) there is an increase in frequency of the nitrogen bonds (NH_2 and NH) in the region 3400-2900 cm^{-1} due to lack of hydrogen bonds, whilst there is a decrease in frequency of the III and IV thioamide bands because of the reaction and formation of complex with copper. Another characteristic peak is around 2560-2590 cm^{-1} that is the S-H stretching bond which however is found solely in the liquid phase. The band is not as intense as the bands of the benzene ring or the N-H bonds, however, it is sharp and substantial and cannot be missed (Smith, 1998: 155). The S-H bond has a strong peak at 3127 cm^{-1}.

Table 6.32. Table with characteristic bands of AMT and AMT solutions in deionised water and ethanol.

GROUP	AMT	0.01M/H_2O	0.01M/ETOH
N-H	3357, 3250, 3127, 2923	3474, 3422, 3308, 3127	3426, 3311, 3168
S-H	3127	-	-
Thioamide band I	1608, 1552	1601, 1504	1600, 1516
Thioamide band II	1361, 1327	1392, 1343	1411, 1342
Thioamide band III	1058	1058	1054
Thioamide band IV	752	680	750 (680)

The reference spectrum of AMT is shown in figure 6.19. The main AMT identification peaks are shown in table 6.32. The S-H bond found at 3127 cm^{-1} was the peak with the higher intensity in the spectrum. Strong peaks of the thioamide bands were found at 1608 and 1552 cm^{-1} for band I, 1361 and 1327 cm^{-1} for band II, 1058 for band III and 752 cm^{-1} for band IV.

The analysis of clean copper coupons treated with 0.01M AMT showed very little absorption and few peaks (the two strong peaks at 2361 and 2340 cm^{-1} were unfortunately humidity from the background) and another at 1177 cm^{-1}. The other peaks were very weak and broad (e.g. 3152- N-H stretching) and the results were inconclusive.

Clean copper treated with combination of BTA + AMT presented a similar picture: strong sharp peaks at 2360 and 2340 (moisture) and some weak broad peaks (e.g. 730 cm^{-1}). Of great interest is the fact that although BTA alone shows a strong spectrum on clean copper, it did not when mixed with AMT. As a result, most of the strong peaks of BTA (e.g. benzene ring at 745 cm^{-1} or N-H and C-H bands) and AMT peaks were missing from this spectrum. Therefore, no conclusions could be drawn on clean copper from reflectance absorbance analysis.

6.11.1.1 Corroded copper

The spectra of corroded copper treated with 0.01M AMT in ethanol or water present essentially the peak shifting described earlier. There was a change in the region 3400-2900 cm^{-1}because of the N-H stretching. More specifically there was a shift towards higher

wavenumbers. The thioamide bands I, III and IV presented a shifting towards lower wavenumber whilst band II increased. Table... shows the shifting of main bands of AMT treatments. As expected, the change of solvent did not cause any significant changes in the spectra. Copper treated with solution of 0.01M AMT in deionised water showed similar results with the coupons treated in AMT in ethanol. The peaks where sharper in the latter, however it is clear that AMT formed a complex with copper in both solvents.

A very strong peak found in these spectra was at 620 (0.01M in ethanol) and 628 in 0.01M in water. This is the peak of cuprite and its presence might lead to the assumption that there was a Cu(I)-AMT complex. Longer periods of time of immersion (24 hours) showed similar results with some peaks presenting higher intensity, without however any great commendable changes with reference to the assignment and position of the bands that remained the same. Figure 6.19 shows the spectra of corroded copper, AMT in KBr, 0.01M in deionised water and 0.01M in ethanol.

Corroded copper coupons treated with different solutions of BTA + AMT present different spectra depending on the concentration of the two compounds in the treatment solution. Copper treated with equimolar solution of BTA + AMT (0.01M) present spectra where AMT peaks were predominant. The same picture was found on coupons treated with 0.1M BTA + 0.01M AMT. The main peaks were the same with some changes in their intensity. More specifically, the spectrum of the treatment with the BTA+AMT equimolar solution has a stronger peak at 1600 cm^{-1}. The second treatment presented some additional peaks, such as 1172 (Cu(I)-BTA), 3359 (N-H stretching) and 991 (Cu(I)-BTA) cm^{-1}. Interestingly

the aforementioned peaks refer to cuprous-BTA complex. In both cases the S-H bond was missing verifying the complexing of AMT with sulphur.

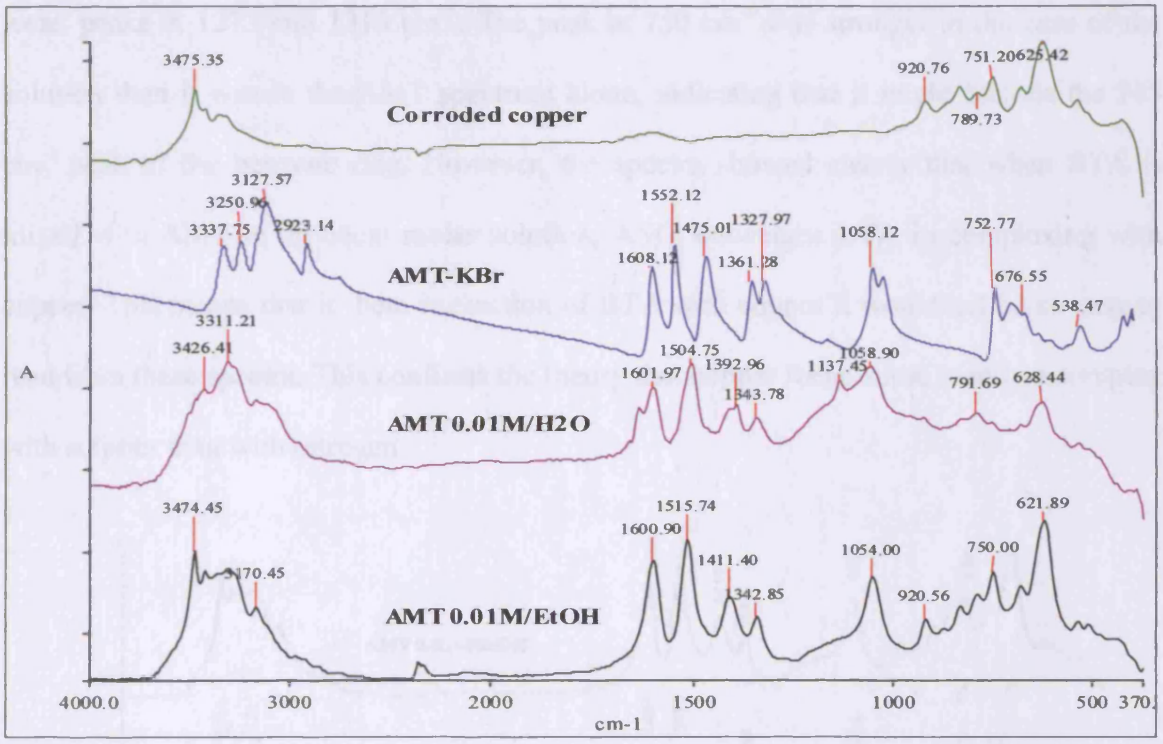


Figure 6-19. FTIR spectra of corroded copper treated with 0.01M AMT in water and in ethanol, AMT, reference spectrum and corroded copper.

Contrary to this, coupons treated with solution of higher BTA concentrations (e.g. 0.25M BTA + 0.01M AMT) BTA bands prevail. Although the latter seems reasonable, the former is found rather interesting. Still the S-H peak at 3127 cm^{-1} was missing showing that apart from the Cu-BTA complex there was a Cu-AMT complex formed as well.

6.11.1.2 0.01M BTA + 0.01M AMT

The spectrum was found to be very similar to that of corroded copper treated with AMT 0.01M. Slight shifting of the peaks was observed (1-2 cm^{-1}) and an AMT peak missing at

2351 cm^{-1}. The main region indicating the presence of BTA was in the region 3500-2400 where the stretching of C-H and intermolecular stretching of NH…N takes place. This was very narrow compared to the BTA spectra. The presence of BTA was evident also through weak peaks at 1273 and 1213 cm^{-1}. The peak at 750 cm^{-1} was stronger in the case of the solution than it was in the AMT spectrum alone, indicating that it might include the 745 cm^{-1} peak of the benzene ring. However, the spectra showed clearly that when BTA is mixed with AMT in an equal molar solution, AMT outweighs BTA in complexing with copper. This means that if there is reaction of BTA with copper it would not be so easy to read from these spectra. This confirms the theory that copper forms more readily a complex with sulphur than with nitrogen.

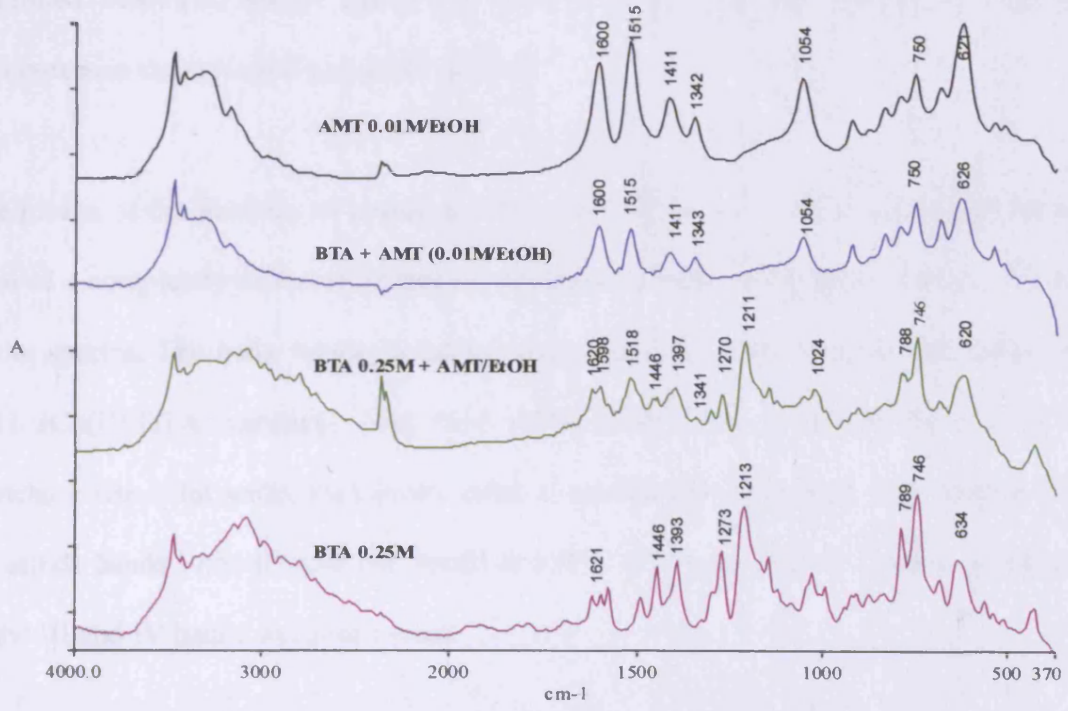


Figure 6-20. Absorption reflectance spectra of corroded copper treated with 0.01M AMT/EtOH, 0.1M BTA + 0.01M AMT/EtOH, 0.25M BTA + 0.01M/EtOH AMT and 0.25M BTA/EtOH.

6.11.1.3 0.1M BTA + 0.01M AMT

The spectra of corroded copper treated with the solution of 0.1M BTA + 0.01M AMT were similar to those of the above-mentioned solution where equal amounts of BTA and AMT were used. Interestingly, the spectra showed that there was definitely a copper-AMT polymeric film formed even when the concentration of BTA is ten times more than that of AMT. This does not mean that there was no Cu-BTA complex formed in addition to the Cu-AMT complex. The latter was also evident from the results of the accelerated corrosion testing where the efficiency of AMT was a lot less than that of the BTA+AMT mixtures. Therefore, copper bonds with both BTA and AMT but from the results it is apparent that these were distinct complexes with each inhibitor separately. Similarly to the previously examined treatment, longer periods of time of immersion did not display significant differences in the collected spectra (Fig. 6.20).

The results of the analysis of corroded copper treated with 0.25M BTA and 0.01M AMT showed a completely different picture to the previous cases. BTA peaks were predominant in the spectra. The main bands found were that of the benzene ring at 746, followed by 1211 (Cu(II)-BTA complex). The band 3500- 2400 cm-1 of the N-H, C-H, NH...N stretching was a lot wider than in the other concentrations examined. The AMT peaks of thioamide bands I and II were still found at 1599, 1517 and 1398 cm^{-1}, however the peaks of the III and IV bands were very weak.

The peak at 3127 cm^{-1} representing the S-H bond was also missing in these spectra illustrating that AMT was also bonding to copper. A longer time of immersion resulted in

similar results, except that the band 3500-2800 that was a lot narrower and the appearance of some weak peaks of Cu(II)-BTA complex (including 1577, 1271, 995 cm^{-1}). It seems that a longer period of immersion resulted in oxidation of some of the cuprous-BTA to cupric-BTA complex in this BTA+AMT combination. This is in agreement with the results of chapter 5 on BTA 0.25M alone, whether longer immersion results in increase of Cu(II)-BTA peak intensity.

A very significant question in this analysis was whether the presence of AMT in BTA solutions influences the structure of the Cu-BTA complexes. As has been discussed in the previous chapter, BTA forms complexes with both cuprous and cupric ions with the former being more stable than the latter. Given that the combination of BTA + AMT proved to be the most successful of those tested and the only combination where there a to be synergism between the two compounds, it is of particular interest to examine whether the presence of AMT affected the Cu-BTA complexing by provoking selective bonding with cuprous ions or in another way. The examination of the non-aqueous solutions that follows was intended to support further the interpretation of the reflectance results by looking into possible reactions (e.g. dissolution of copper and reaction with AMT and or BTA) taking place at different periods of time.

The analysis of the BTA + AMT solutions did not reveal any significant information. There was only a weak peak was found at 2575 cm^{-1} (thiol of AMT).

6.11.2 BTA + BZA

BZA is a primary aromatic amine and its spectrum is characterised by the stretching of the NH_2 functional group of its molecule. The main identification bands of primary aromatic amines are that of N-H_2 stretching at 3370-3170 cm^{-1}, N-H deformations at 1650-1580 and 895-650 cm^{-1}, C-N stretching broad band at 1090-1020 cm^{-1} (Burns and Ciurczak, 2001).

Unfortunately, the analysis of copper treated with BZA did not reveal any significant results regarding the reactions taking place between copper and BZA.

A first look at the spectra of clean copper treated with BTA + BZA solutions showed that BTA peaks (e.g. 745 cm^{-1}) are still predominant. The coupons treated with equimolar solutions of BTA + BZA showed more BZA peaks than the those treated with 0.25M BTA + 0.1M BZA in ethanol. The N-H stretching at 3370-3160 cm^{-1}, at 1578 and 1493 and cm^{-1} and a strong 698 peak all corresponding to the N-H deformation vibration of BZA were found. As the concentration of BTA increased the peaks of BZA diminished (Fig. 6.21).

The analysis of corroded copper treated with BZA showed similar results to those observed on clean copper. The presence of BZA was evident only through selected peaks such as 698 cm^{-1} and some peaks in the region of 1580-1490 cm^{-1} where N-H deformation takes place. The treatment of 0.1M BTA + 0.1M BZA in deionised water presented more BZA peaks than the others. The increase in BTA concentration and the change of solvent from water to ethanol seemed to affect the formation of the complex formed on the surface, with Cu-BTA being predominant.

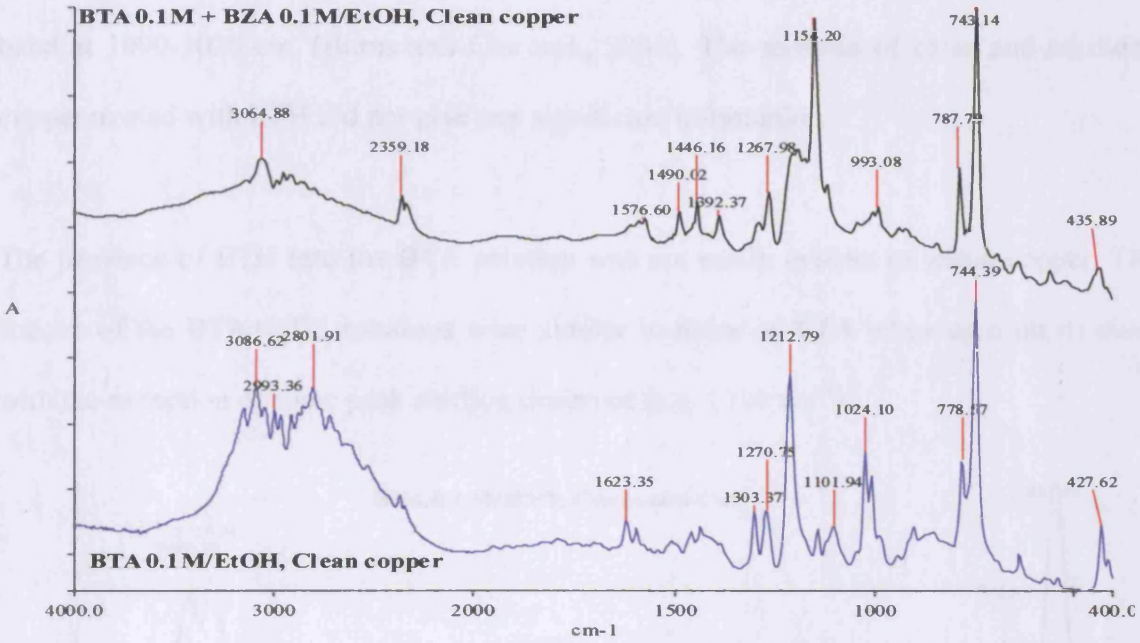


Figure 6-21. FTIR spectra of clean copper showing the effect of BZA on the Cu-BTA film formation.

Another interesting aspect was whether BZA affected the way BTA complexes with copper. There seemed to be only few changes. These were more evident in the region of 895-700, which appears in case of BTA + BZA wider and less defined than when BTA was used alone. Other minor changes were observed in the presence of weak BZA peaks (such as the C-N stretching bond at 1123 cm^{-1}).

The examination of the BTA peaks showed the presence of a cupric complex on the surface.

6.11.3 BTA + ETH

Ethanolamine is like BZA a primary amine as well as a primary alcohol. The functional groups characterising ETH are similar to those of BZA, the bands of N-H_2 stretching at

3370-3170 cm^{-1}, N-H deformations at 1650-1580 and 895-650 cm^{-1}, C-N stretching broad band at 1090-1020 cm^{-1}(Burns and Ciurczak, 2001). The analysis of clean and corroded copper treated with ETH did not give any significant information.

The presence of ETH into the BTA solution was not easily evident on clean copper. The spectra of the BTA+ETH solutions were similar to those of BTA when used on its own, with the exception of some peak shifting observed (e.g. 1209 cm^{-1}).

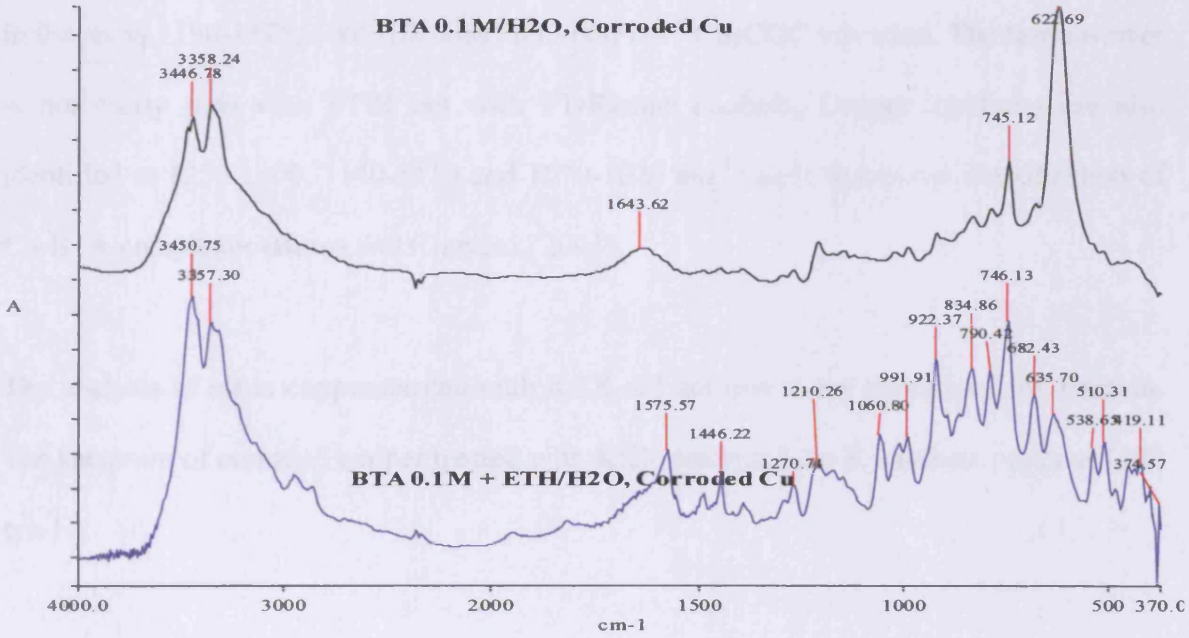


Figure 6-22. Spectra of 0.1M BTA with and without the addition of 0.1M ETH in deionised water.

The spectrum of corroded copper treated with 0.1M BTA + 0.1M ETH revealed that the addition of ETH into BTA enhanced somehow the bonding of BTA with copper. Only a few peaks correlated to ETH, whilst there were a lot of new peaks corresponding to Cu(II)-BTA complex such as the peak at 1176, 1575 cm^{-1} and to Cu(I)-BTA at 991 and 1270 cm^{-1} peaks that were not present when 0.1M BTA in deionised water was used alone (Fig. 6.22).

The spectrum of the BTA + ETH in ethanol was similar to the spectrum of BTA 0.1M in ethanol. The use of water as a solvent resulted in less BTA peaks. Another difference between the spectra was found in the area of NH stretching (3600-2800 cm^{-1}) which was very narrow and also had peaks missing.

6.11.4 BTA + KEX

The IR identification of xanthates is based on the identification of the C=S bond with strong peaks at 1065-1040 and 1250-1100 cm^{-1}. Potassium xanthates present strong peaks in the areas 1190-1175, 1065-1020 and 630-600 cm^{-1} CS_2COC vibration. The last however is not easily seen with FTIR but with FT-Raman analysis. Copper xanthates are also identified at 1250-1200, 1140-1110 and 1070-1020 cm^{-1} bands that allow identification of Cu-BTA complexes (Burns and Ciurczak, 2001).

The analysis of clean copper treated with KEX did not reveal any significant information. The spectrum of corroded copper treated with KEX presented the K xanthate peaks at 1190 cm-1.

Clean copper treated with 0.25M BTA + 0.1M KEX presented an interesting mixture of KEX and some BTA peaks. The strongest peaks were those at 1469 and 1394 which are of indicating a CuI-BTA complex, followed by a peak of copper xanthate at 1119 cm^{-1} and a very strong peak at 627 cm^{-1} which is most probably cuprite. There were also strong peaks at 3467 and 3355 cm^{-1}, indicating NH stretching bonds of BTA.

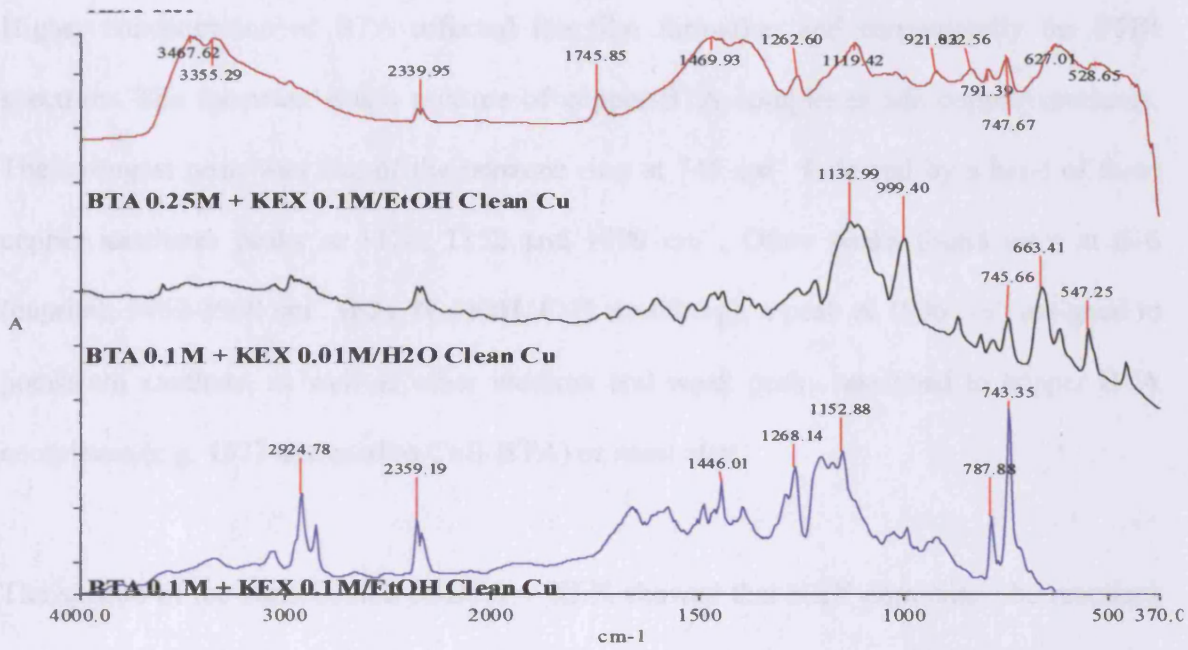


Figure 6-23. FTIR spectra of KEX and BTA+ KEX treatments applied on clean copper.

The spectra of corroded copper treated with BTA + KEX solution in different solvent illustrate the effect the solvent has on the film formation. The spectra had little resemblance to those of BTA or KEX treated copper. The stronger peak found on a copper sample treated with 0.1M BTA + 0.1M KEX in deionised water was that of copper-xanthates at 1211 1051 and 1129 cm^{-1}. Some of these peaks are also found in literature as Cu(II)-BTA (1211) and Cu(I)-BTA (1051), however, the sequence and intensity of the peaks demonstrate they are copper xanthates, not copper-BTA complexes. This is confirmed by the weak peak of benzene ring at 752 cm^{-1} (shift of the peak from 745 cm^{-1}). The same solution in ethanol presented a similar picture although with lower intensity of the peaks (Fig. 6.23).

Higher concentration of BTA affected the film formation and consequently the FTIR spectrum. The spectrum was a mixture of copper-BTA complexes and copper xanthates. The strongest peak was that of the benzene ring at 745 cm^{-1} followed by a band of three copper xanthates peaks at 1124, 1152 and 1199 cm^{-1}. Other peaks found were at 616 (cuprite), 3469-2900 cm^{-1} (NH, N..HOH, C-H stretching), a peak at 1006 cm^{-1} assigned to potassium xanthate, as well as other medium and weak peaks assigned to copper BTA complexes (e.g. 1577 assigned to CuII-BTA) or xanthates.

The spectra of the combination of BTA + KEX showed that KEX dominates the reactions with copper by forming copper xanthates. Complexes of copper with BTA were also present however the intensities of their peaks were not as strong in this case. The film formed on the copper surface when BTA is mixed with KEX appeared thicker than that of BTA as it can be also seen from the SEM images. The results of the analysis clearly indicate the presence of both inhibitors, however it is not clear whether there was one polymeric film or two complimentary polymeric films.

6.11.5 BTA + KI

The main identification bands of metals with halides are in the near infrared region. There is a stretch at 360-150 cm^{-1} and a deformation at 100-30 cm^{-1}. Unfortunately the analysis was carried out in the mid infrared region so the analysis focuses more on the effect KI had on the copper-BTA complex formation.

The analysis of clean and corroded copper immersed in KI solutions showed strong water absorption and in case of corroded copper (I) oxide (cuprite) at 624 cm^{-1} and copper II oxide (tenorite) at 482 cm^{-1}.

The spectrum of clean copper treated with 0.1M BTA + 0.01M KI clearly illustrated the formation of copper-BTA complexes with benzene ring being the strongest peak. Cu(I)-BTA complex is indicated by the peaks 1152, 1446, 1489 and Cu(II)-BTA complexes as the 1575, 1394 and 994 cm^{-1} indicate. The existence of iodide complexing with CH_2 and CH_3 might be evident through the peaks 1204, 1268, 1177 cm^{-1} where the CH_2 wagging vibration takes place. These peaks could indicate the formation of a copper-iodide-BTA complex. An interesting change was found in the 3500-3200 cm^{-1} region where there were no strong peaks. The lack of peaks in the area with N-H bonds may be indicative of more Cu-N bonding taking place.

The analysis of sample treated with 0.25M BTA + 0.1M KI showed similar peaks to those mentioned above. The main difference found was related to the definition of some of the peaks. The strongest peak was also that of the benzene ring of BTA. There is also a broad area with peaks of CH_2-I (1208-1126, 1267 cm^{-1}). It appeared that copper(I)-BTA was predominant even in this treatment. The main difference was the presence of cuprite peak at 623 cm^{-1}.

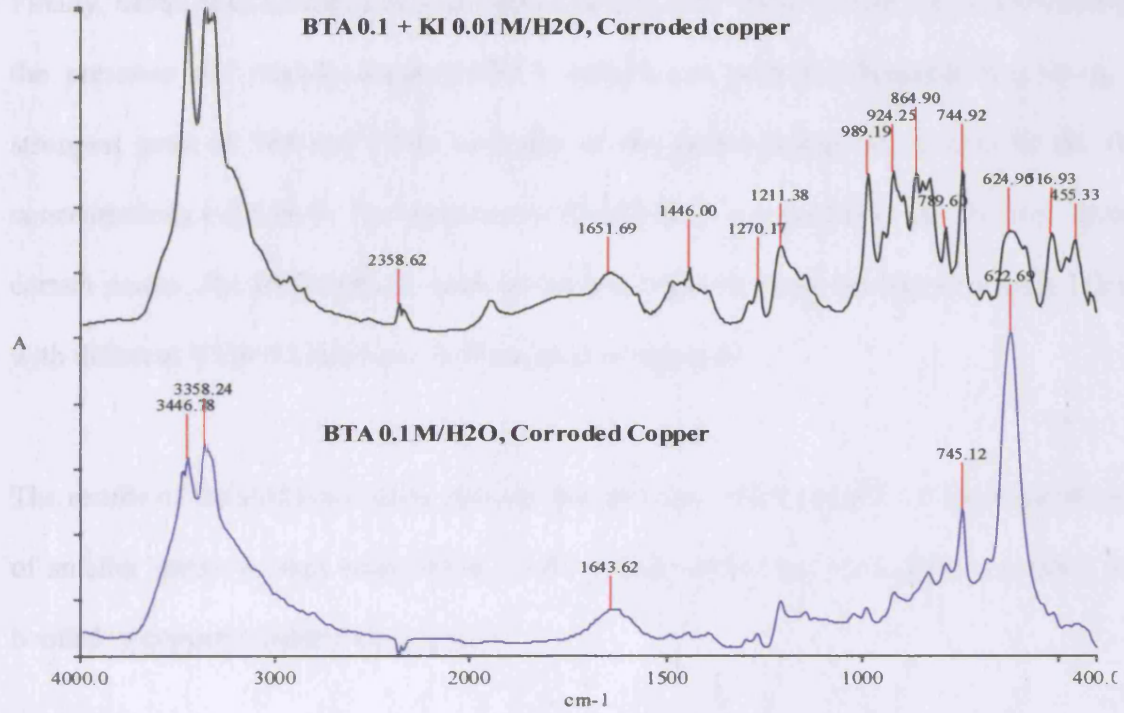


Figure 6-24. FTIR comparison between 0.1M BTA/H2O and 0.1M BTA + 0.01M KI/H2O applied on corroded copper.

Corroded copper treated with 0.01M BTA + 0.01M KI in water showed a rather different picture than those previously observed. The strongest peaks found were broad peak areas such as 990-848 and 599-496 cm^{-1} that were unidentified copper-BTA complexes. The presence of BTA was also evident through the benzene ring at 741 cm^{-1}. There were also peaks indicating CH bonds with iodide like those at1279, 1228 and 1152 cm^{-1}.

The spectrum of corroded copper treated with 0.1M BTA + 0.01M KI showed strong copper I oxide peak at 624 cm^{-1}, followed by the benzene ring peak at 745 cm^{-1}. The predominant complex of BTA found was that of Cu(I)-BTA as indicated by the peaks 1610 and 1447 cm^{-1}(Fig. 6.24).

Finally, samples of corroded copper treated with 0.25M BTA + 0.1M KI clearly illustrated the presence of mainly copper(I)-BTA complexes, with the benzene ring being the strongest peak at 744 cm^{-1}. The intensity of the peaks change in relation to the other concentrations examined. The presence of Cu(II)-BTA complexes is also evident through certain peaks. The difference in peak intensities between corroded copper samples treated with different BTA+KI solutions is illustrated in Appendix 5.

The results of the analysis clearly indicate the presence of copper-BTA complex with peaks of smaller intensity than when those of BTA alone. In most cases, BTA appeared to be bonded to copper I rather than copper II.

6.11.6 BTA + PMT

PMT in different concentrations such as 0.005M in deionised water and ethanol and 0.1M in ethanol were initially analysed for comparative reasons. The main identification bands of PMT are 3018, 2894, 2745 cm^{-1} representing the CH and NH bond stretching, 2541 (stretching of SH), vibrations of tetrazole ring at 1594, 1381, 1353, 1316, 1092 and 1072 cm^{-1}. Vibrations of the phenyl ring are found at 1594, 1491 and 1455 cm^{-1}. The four thioamide bands are found at 1491 (band I), 1297 and 1275 cm^{-1} (band II), 991 and 906 (band III) and 808 and 751 cm^{-1} (band IV). Other peaks are 1210, 1156 and 1050 cm^{-1} representing several CH, CN, CS bonds. The complexing of PMT with copper affects the thioamide bands. Depending on the peaks present, their shifts and intensity, one can find whether there is bonding through nitrogen or sulphur. For example, positive shifting of thioamide band I and a negative shift of bands II, III and IV are indicative of bonding of

PMT to copper through both N and S. The absence of N-H and S-H (1587 cm^{-1}) bonds also indicate the formation of a copper-PMT complex through both the nitrogen and the sulphur of the molecule (Ye *et al*, 1998).

The analysis of clean copper treated with PMT did not present any results of significance worth mentioning results because of high reflectance of the clean copper surfaces. Corroded coupons treated with PMT showed a shift of certain peaks, due to bonding with copper. The lack of the 2541 cm^{-1} peak of S-H bond clearly indicated bonding of copper with S. The changes of the thioamide bands in the fashion described above also showed bonding of PMT through both nitrogen and sulphur. The same PMT concentration dissolved in deionised water had a peak which presented a different picture. There seemed to be a significant change in the formation of the Cu-PMT film when water was used a solvent. There were only a few weak peaks in the area 1600-930 cm^{-1}. All the peaks for the phenyl ring and tetrazole ring stretching were missing whilst the strongest peak was that of cuprite at 625 cm^{-1}. It is not very clear whether the bonding between copper and PMT took place through S or N in this case.

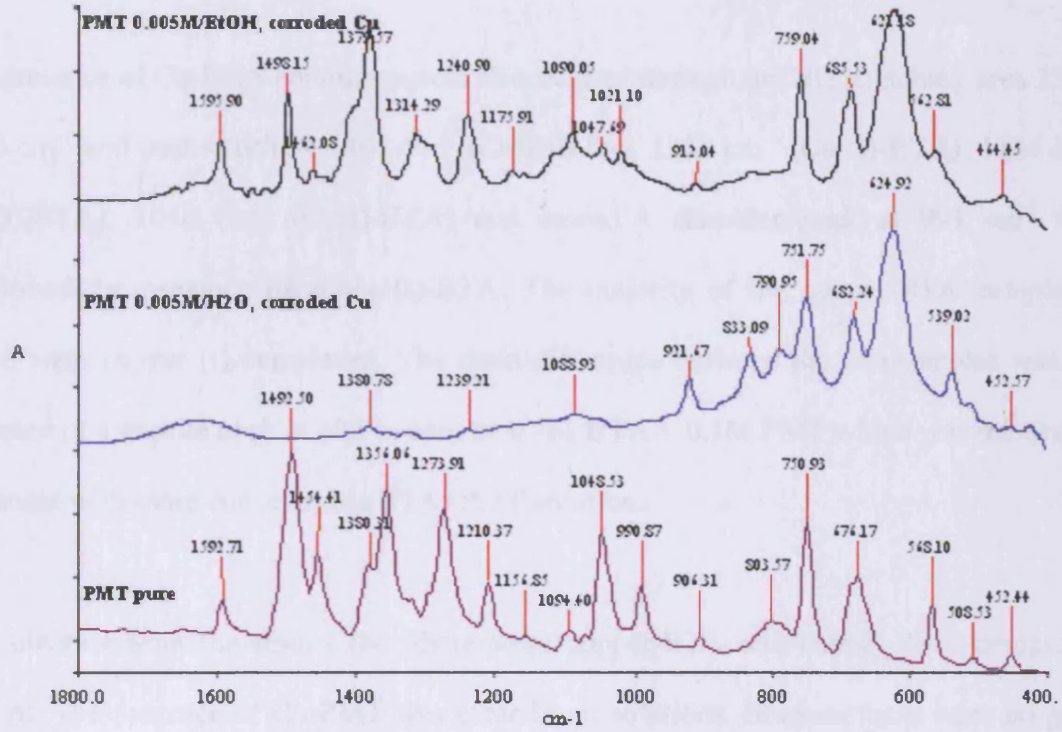


Figure 6-25. FTIR spectra of PMT: reference and corroded copper treated with 0.005 PMT/H2O and 0.005M PMT/EtOH showing the effect of the solvent on the Cu-PMT film formation.

The analysis of clean coupons treated with BTA+PMT was not conclusive. There were only few wide peaks that could not be assigned to BTA or PMT. On the contrary, the spectra of corroded copper samples treated with BTA+PMT presented peaks of both PMT and BTA complexes with copper. The spectra of coupons treated with BTA+PMT solutions (0.25M BTA+ 0.1M PMT in ethanol and 0.1M BTA + 0.1M PMT in ethanol) were similar in illustrating the presence of BTA and PMT complexes with copper. The strongest peak was that of the benzene ring at 747 and 751 cm^{-1} respectively followed by two PMT peaks at 1376 cm^{-1} (tetrazole ring vibration) and 1498 cm^{-1} of the thioamide band I. Other intense peaks were at 1212 cm^{-1} (that could be attributed to both CuII-BTA and Cu-PMT), 1595 (vibration of the phenyl ring),

Figure 6.25 shows the spectra of PMT and BTA+PMT treatments.

The presence of Cu-BTA complexes was also evident through the NH stretching area 3500-2800 cm^{-1} and peaks such as 1446 cm^{-1} (Cu(I)-BTA), 1212 cm^{-1} (Cu(II)-BTA), 1144 cm^{-1} (Cu(I)-BTA), 1046 cm^{-1} (Cu(I)-BTA) and more. A shoulder peak at 991 cm^{-1} also confirmed the presence of copper(I)-BTA. The majority of the copper-BTA complexes found were copper (I) complexes. The main difference between the two samples was the presence of a cuprite peak at 625 in case of 0.1M BTA + 0.1M PMT which was missing in treatment with more concentrated BTA+PMT solution.

It is obvious from the results that there were copper-BTA and copper-PMT complexes present. The presence of Cu-PMT was clear in all solutions. Because there were no great changes in peaks positions especially for PMT, it is assumed that there were individual complexes that may or may not have formed one coordinated film. This is an assumption that cannot be easily confirmed with FTIR. The presence of PMT in the BTA solutions affected the copper-BTA formation with Cu-I prevailing.

The results of FTIR showed the way that the compounds interact with copper when used alone or in combination with BTA. In all cases, the presence of both compounds was identified. The way concentration affects the film formation is evident in different examples. For example, the spectra of BTA + AMT showed that there is AMT bonding with copper which was found predominant in most solutions. Another interesting point is how the addition of a second compound affected the Cu-BTA film formation. In most treatments, the second compound had a great effect on the spectra, dependent on the

substrate, concentration of the solution and the solvent. Further analysis of coupons with XPS verified or complemented these results.

6.12 X-Ray Photoelectron Spectroscopy (XPS) of combinations

The XPS analysis was carried out to gain information about the chemical nature of the complexes formed on copper by the different inhibitors. More specifically, the analysis would help understanding the way each compound reacts with copper, whether it complexes with copper I or copper II, how the combination of these compounds with BTA affects the reactions and the bonding with copper as well as the relationship of the complexes to the efficiency of the tested treatments observed and discussed earlier in this chapter.

Clean and corroded copper coupons treated with the compounds alone were analysed and these analyses are at the beginning of each section, followed by analysis of coupons treated with selected solutions of their combination with BTA. XPS is an expensive and time-consuming technique thus, the majority but not all of the tested solutions were analysed. The XPS results of untreated clean and corroded copper and copper treated with BTA solutions examined in chapter 5 were used as reference for comparative reasons.

A selection of the combinations were also analysed on glass slides. However the analysis did not give important information about the elements, as it also includes in the results the glass slide itself.

Clean untreated copper, being very reactive, is covered with a thin layer of copper oxides, copper I oxide prevailing. Corroded copper analysed showed Cu_2O, CuO and CuCl as well as some hydroxyl/water clusters present (see chapter 5).

6.12.1 XPS of BTA + AMT

6.12.1.1 AMT

AMT is a nitrogen and sulphur-containing compound the efficiency of which as a corrosion inhibitor for copper has been reported in several studies. AMT is bonded to copper through sulphur and/or nitrogen of its molecule which represent the inhibitor in the analysis (see Chapter 3).

The analysis of clean copper treated with AMT showed that AMT forms a complex mainly with copper(I). Copper(II) was also found as indicated by the weak peak at a Binding Energy (BE) of 934.8eV and satellites. The Cu^{+}/Cu^{++} area ratio was found 3.4.

The spectra of corroded copper treated with AMT showed that AMT is bonded to copper(I). There were some small differences between the spectra of corroded copper treated with AMT in different solvents. Higher concentrations of nitrogen, sulphur and copper were found on coupons treated with AMT in ethanol whilst coupons treated with AMT in water presented higher oxygen and chloride content.

The comparison between clean and corroded copper spectra showed that the copper-AMT film formed varies depending on the substrate. Clean copper treated with AMT presented a higher percentage of oxygen and carbon and lower sulphur than corroded copper. The semi-

quantified results and the calculated area ratio between copper(I) and copper(II) are shown in table 6.33.

6.12.1.2 BTA +AMT

The next set of samples analysed were those of coupons treated with selected BTA + AMT solutions. Clean copper treated with 0.1M BTA + 0.01M AMT in ethanol has both copper I and copper II peaks, with copper II being predominant as it is also indicated by the strong satellite peaks. The Cu^{+}/Cu^{++} area ratio was found 0.6. It is important to mention that clean copper treated with 0.1M BTA/EtOH presented both copper (I) and (II) peaks and strong copper(II) satellites. Copper I was higher than copper II with Cu^{+}/Cu^{++} area ratio being 2.3. Nitrogen is increased in the combined BTA and AMT treatment in relation to that found on coupons treated with AMT alone (24 and 13 % respectively) however it is still at similar levels to that of BTA 0.1M used alone. The sulphur percentage is lower than that of AMT alone (5.5 and 7.7% respectively).

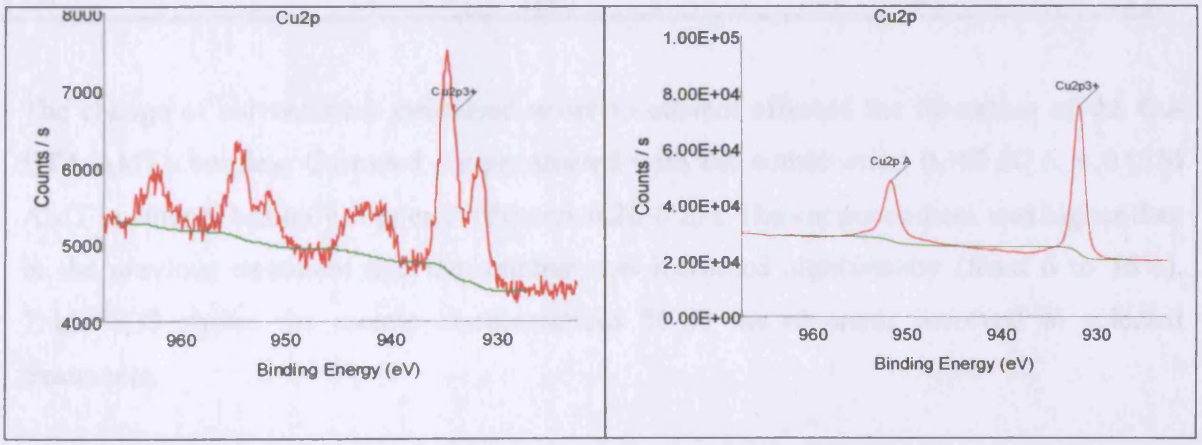


Figure 6-26. Clean copper treated with 0.1M BTA and 0.01M AMT in ethanol. Both copper I and copper II can be seen with the latter being predominant as indicated by the intensities and the strong copper II satellite peaks.

Figure 6-27. Corroded copper treated with 0.1M BTA and 0.01M AMT in ethanol. There is only copper I in this sample.

Corroded copper treated with 0.1M BTA + 0.01M AMT in water showed copper I predominantly. The Cu^{+}/Cu^{++} ratio was found to be between 2.4-2.8. BTA 0.1M in water has mainly copper II with very little copper I (ratio 0.04) therefore the presence of AMT is prevalent in this process resulting in the formation of a CuI-BTA-AMT complex. Because of the higher BTA concentration in the BTA + AMT solution it could be assumed that copper BTA would be more readily bonded to copper with the Cu-BTA complex being easily identifiable, copper is preferably bonded to sulphur of AMT. It seems that both of the complexes exist (Cu-BTA and Cu-AMT) with AMT clearly affecting the overall process.

Table 6.33. Semi-quantitative XPS data of corroded coupons treated with AMT, BTA and BTA-AMT solutions. * Nitrogen and carbon found are due to contamination of the samples.

TREATMENT	CLEAN CU	CORRODED CU	AMT 0.01M/ H_2O	AMT 0.01M/ ETOH	BTA 0.1M/ H_2O	BTA 0.1M/ ETOH	BTA 0.25M/ ETOH	BTA 0.1M+ 0.01M AMT/H_2O	BTA 0.1M+ 0.01M AMT/ ETOH	BTA 0.25M+ 0.01M AMT/ ETOH
Element	At. %									
Cu2p	6.5	17.2	3.9	15.9	6.7	6.8	2.9	4.5	8.9	4.2
C1s	11.2*	24.1*	32.4	26.3	66.7	64.3	66.4	58.6	45.5	62.4
N1s	1.3*	2.5*	23.0	26.9	23.7	24.0	27.3	28.2	23.4	23.7
Cl2p	-	18.5	8.6	4.3	1.7	4.0	3.3	1.6	1.8	1.3
O1s	15.9	37.7	14.3	3.8	1.2	1.0	0.1	1.3	4.7	3.1
S2p	-	-	17.8	22.9	-	-	-	5.8	15.7	5.3

The change of solvent from deionised water to ethanol affected the formation of the Cu-BTA-AMT complex. Corroded copper treated with the combination 0.1M BTA + 0.01M AMT in ethanol has only copper(I) (Figures 6.26-6.27). The copper content was higher than in the previous treatment and the sulphur was increased significantly (from 6 to 16%). Table 6.33 shows the atomic concentrations % of the elements involved in selected treatments.

Copper treated with 0.25M BTA + 0.01M AMT in ethanol showed both copper (I) and (II) peaks with the former being predominant (Cu^{+}/Cu^{+2}=3.6). The chloride content was very low (<2at%) and whilst the carbon content increased and the nitrogen remained in the same

levels as in 0.1M BTA + 0.01M AMT in ethanol but the sulphur content decreased significantly. A very interesting outcome of the analysis is related to the chloride content which was found in all treatments less than 2at%, was less than that found on untreated corroded copper (approx. 5at%), treated coupons with BTA (3- 4at%) or AMT (3-4at%).

The XPS data show that although AMT is in a very low concentration compared to that of BTA, there is still a Cu-AMT complex formed on the surface. These results are of particular interest especially when coupled with the FTIR results. The most successful solution (0.1M BTA and 0.01M AMT in ethanol) showed higher sulphur than the other BTA + AMT combinations.

All the XPS spectra and semi-quantitative tables are found in Appendix 6.

6.12.2 XPS of BTA + BZA

6.12.2.1 BZA 0.1M clean and corroded copper

The analysis of clean and corroded copper treated with BZA showed a high oxygen content and low nitrogen (4at%). In particular, on clean copper BZA is bonded to both copper(I) and copper(II) with the former prevailing. The copper atomic concentration percentage was very high compared to other treatments (16at%) and the Cu^{+}/Cu^{++} ratio was found to be 1.8. Oxygen has a very strong peak at 531 with a weak satellite peak at 536 which is also found on untreated clean copper. The high oxygen content (44at%) and the peak at 531eV indicate the presence of oxide and hydroxyl (possibly water clusters from the environment). Corroded copper treated with BZA showed strong copper(II) satellites. The nitrogen concentration was also low (approx 9at%). Chloride content was found to be almost 11at%,

a lot higher than in other treatments, still lower than the percentage found of untreated corroded copper (18at%). The oxygen content was also found to be quite high compared to others (16at%).

BZA has been reported to form a cupric-BZA complex (Fleischmann *et al*, 1983: 1325). Whilst this is the case for corroded copper, clean copper has both copper oxidation states, with cuprous being predominant.

6.12.2.2 BTA + BZA

The analysis of clean copper treated with BTA 0.1M + BZA 0.1M in ethanol showed that predominantly copper II is bonded to the inhibitive compounds. The Cu^{+}/Cu^{++} ratio was 0.4. The nitrogen content was high and oxygen very low, corresponding to the values of BTA alone.

On corroded copper, the results also showed mainly copper(II). The Cu^{+}/Cu^{++} ratio was found to be approximately 0.2. Interestingly there is very low oxygen and chloride content (less than <1at%). Corroded copper treated with the combination dissolved in deionised water presented results similar to those of the same solution in ethanol. The main difference found was the oxygen and chloride contents were slightly higher (1.5at% approx). Copper(II) is predominant with Cu^{+}/Cu^{++} ratio 0.3.

The analysis presents interest in terms not only of the oxidation state of copper, but also because of the atomic concentration percentages that vary so much from BZA to combined solutions with BTA or BTA alone. The results of the combinations were closer to those of BTA than BZA alone.

6.12.3 XPS of BTA +ETH

6.12.3.1 ETH

The spectra of clean and corroded copper treated with 0.1M ethanolamine (ETH) in ethanol presented very strong oxygen peaks at 530eV in high concentrations (30at% and 20at% respectively). The results of the analysis showed that ETH forms a complex with copper II in both copper substrates. The atomic percentage of copper was found to be around 9at% and the nitrogen content around 16at% on both substrates. It was mentioned during the first experiment of ETH that there was partial etching of the surface of corroded copper caused by ETH. However, the concentration of chloride found on the coupon was around 19at%, similar to that of untreated copper nevertheless a lot higher that the other treatments. A possible explanation might be that ETH removed the corrosion layer unevenly, or that it caused etching of the cuprite layer exposing the nantokite underneath. In the former case, the sample was taken from an area with corrosion layer. From the results it appears that the complex formed is a copper(II)-ETH incorporating chlorides and oxygen in its structure.

6.12.3.2 BTA + ETH

The analysis of clean copper treated with 0.1M BTA + 0.1M ETH in ethanol showed a very strong copper II peak at 935.6eV and a weak copper I peak at 932.5eV. The Cu^{+}/Cu^{++} ratio was found to be 0.3. There was low oxygen content (1.4at%). The percentages of carbon and nitrogen were also high (63 and 29at%). More concentrated solutions of 0.25M BTA + 0.1M ETH in ethanol showed similar results. There was mainly copper(II) with Cu^{+}/Cu^{++} ratio of 0.15. The nitrogen content was also 29at%.

Corroded coupons treated with 0.1M BTA + 0.1M ETH in deionised water showed both copper I and copper II, with copper II being higher compared to copper I. The Cu^{+}/Cu^{++} ratio was found to be 0.7. Although ethanolamine alone seems to result in high oxygen and chloride content, the analysis of the combination treatment showed low oxygen and chloride content. The nitrogen content was also very high (25at%) as well as carbon (66at%).

The analysis of the same solution in ethanol showed a small deviation from the results of the same solution in water. There was mainly copper II with a very weak peak of copper I. The copper content was very low (<1at%) and no chloride was detected. Oxygen levels were also low (2at%), whilst carbon and nitrogen were very high (68 and 29at% respectively). This was the main difference observed between the two treatments. Nitrogen concentration was found almost twice as much in the ethanol treatment (from 14.4at% in water to 27.5at% in ethanol). The Cu^{+}/Cu^{++} ratio was less than 0.1. The change in the nitrogen content and reduction in the chloride and oxygen concentrations confirmed that the solvent affected indeed the reactions between copper and the inhibitors used.

The results for corroded coupons treated with 0.25M BTA + 0.1M ETH in ethanol were similar to those of 0.1M BTA + 0.1M ETH in ethanol. There was mainly copper II with a Cu^{+}/Cu^{++} ratio that was also less than 0.1. Carbon and nitrogen content were very high whilst chlorides (<0.2at%) and oxygen (1at%) were very low. Chloride content was very low, below the detection limits of the technique.

6.12.4 XPS of BTA + KEX
6.12.4.1 KEX

Clean copper treated with 0.1M KEX in ethanol presented only copper(I) peak. Oxygen was found in high concentration (20at%) however the peak was wide and not very defined. Sulphur was found in an atomic concentration of 22at%.

Corroded copper treated with the same solution also presented copper(I) peak however the difference here was in the atomic concentrations of the elements. Copper was found to be 21at%, which was higher than that found on untreated copper, sulphur 41at%, oxygen 20at% and chloride 1at%. The spectra of 0.1M KEX in water were quite similar to those of 0.1M KEX in water. The main difference observed between the two treatments was related to the concentration of some elements. Sulphur and copper were lower in this case and the concentration of chlorides increased. In both cases oxygen was quite high, with its concentration being slightly lower in the aqueous treatment.

It is worth noting that oxygen is part of the KEX molecule as with ETH, unlike all the other compounds tested. Therefore the high oxygen levels found in the KEX treatments are attributable to that. Carbon content was significantly lower in all KEX and BTA + KEX treatments.

Angle resolved measurements were also carried out on corroded copper treated with 0.1M KEX in ethanol samples. There were no great differences at the two different angles the sample was examined. Interestingly, although there was more copper and less carbon when the sample was tilted, the concentration of sulphur remained unvarying.

6.12.4.2 BTA + KEX

The XPS analysis of the coupons treated with BTA + KEX showed that the film formed is dependent on the concentration of the solution. Clean coupons treated with 0.1M BTA + 0.1M KEX in deionised water, were covered with a copper I complex. There was also high concentration of oxygen (18at%) and sulphur was at around 15at%. Nitrogen content was found substantially low (9at%) especially when compared to 0.1M BTA results (23at%).

Table 6.34. XPS semi-quantification of atomic concentrations of BTA, KEX and BTA+KEX treatments.

TREATMENT	0.1M KEX/ H_2O	0.1M BTA/ H_2O	0.25 M BTA/ ETOH	0.1M BTA + 0.1M KEX/ H_2O	0.25M + 0.1M KEX/ ETOH	0.1M KEX/ ETOH	0.1M KEX /H_2O	0.1M BTA/ H_2O	0.25M BTA/ ETOH	0.1M BTA + 0.1M KEX/ H_2O	0.25M + 0.1M KEX/ ETOH
Element	Clean copper (At%)					Corroded copper (At%)					
Cu2p	5.5	7.6	2.5	10.3	1.2	21.7	17.5	7.9	2.9	19.7	5.5
C1s	33.7	67.2	66.7	36.6	51.8	10.8	21.0	65.9	66.4	19.3	42.4
N1s	2.1*	21.5	24.6	8.6	18.4	-	5.8*	23.7	27.3	6.9	14.4
Cl2p	-	-	-	-	-	1.2	3.4	1.8	3.3	4.1	5.2
O1s	19.5	3.7	6.2	16.5	6.5	20.7	16.4	0.8	0.1	15.3	9.0
S2p	22.1			14.3	4.9	41.4	31.0			31.4	10.8
K2s	8.0			5.0	6.9	0.3	1.7			1.8	5.0
K2p	9.0			8.8	10.3	4.1	3.1			1.8	7.9
* Nitrogen is due to surface contamination.											

The increase in BTA concentration in the same combination (0.25M BTA and 0.1M KEX in ethanol) showed that clean copper was covered with a copper II complex. Copper was found in very low concentration (1.2at%). In general, there were big differences between the two BTA + KEX solutions. The amount of nitrogen was increased whilst sulphur and oxygen were decreased significantly. The concentration of potassium was also increased (Fig.6.34).

The analysis of the inhibitor films formed on corroded copper treated with both solutions of BTA + KEX examined showed that there is only copper I complexes on the surface as it is also confirmed by the absence of copper II satellites. However, the films formed by the

different solutions were different indicating that concentration and possibly solvent influence the composition and structure of the polymeric film formed. The analysis of 0.1M BTA + 0.1M KEX in water applied on corroded copper showed high copper, sulphur and oxygen concentrations (19.6, 32 and 15.6at% respectively) and low nitrogen (7at%). In the case of 0.25M BTA and 0.1M KEX in ethanol, copper, sulphur and oxygen were significantly lower (5.5, 10.8 and 8.9at% respectively) whilst the concentration of nitrogen was increased to 14at%.

6.12.5 XPS of BTA + KI

6.12.5.1 KI

The results of the analysis show that there is a CuI (copper iodine) formed on the surface as it is clearly indicated by the copper (932eV) and iodide (619.4eV) peaks for both clean and corroded coupons immersed into aqueous potassium iodide solutions. The atomic concentrations on clean copper indicate high iodide (15at%) and potassium content (6at% K2s and 9at% for K2p) and oxygen (32at%). Copper was mainly copper(I) with some copper(II) also present as also indicated by the copper(II) satellites. The copper content was 9at%, higher than that of untreated clean copper (6.5at%).

KI on corroded copper had a different effect. Copper(I) is predominant, with some copper(II) also present. The atomic concentrations present particular interest as the iodine content was found to be around 55at%, whilst the potassium was a lot lower than on untreated copper (K2p was 3at% and K2s was 2at%). The copper content was around 7.8at%. Oxygen was also present in high percentage (19at%). It appeared that there was a lot of excess iodide on the surface of the sample.

This iodide content shows that there was definitely a reaction between copper and iodine, clearly indicated by the formation of copper iodide. This could be either adsorbed on the copper substrate or it might have formed a surface layer. This is of particular interest for the analysis of its combination with BTA.

6.12.5.2 BTA + KI

Clean copper treated with BTA + KI solutions presented both copper oxidation states with copper II being predominant. The Cu^{+}/Cu^{++} area ratio was found to be 0.4-0.6, but its content was very low (0.8-1.2at%). Another interesting area was the atomic concentrations of the elements involved. Potassium was a lot lower than what had been observed in KI treatments and iodine was at 13at%. The nitrogen peak was at 399.5eV and around 24.5at%. Oxygen was also low (2-2.6at%). The binding energies of iodide and copper(I) showed that copper iodide formed on the surface.

The spectra of corroded copper treated with BTA + KI treatments showed interesting results. Coupons treated with 0.1M + 0.1M KI in deionised water most probably had Cu(I)-I-BTA formed. The copper percentage was 3.8% and the Cu^{+}/Cu^{++} area ratio was 3.4. The nitrogen content was around 20at% and the iodide at 27at%. The potassium and chloride contents were below the detection limits of XPS (<1at%).

Corroded copper treated with 0.25M BTA + 0.1M KI presented a different picture. Copper was too low to be detected. It appeared that copper was present in the cuprous form. The atomic concentrations of the elements were the most interesting as nitrogen was found to be

5at%, oxygen 6at%, potassium 2 and 5at% (K2s and K2p respectively) chloride was below detection limits and iodide 62at%.

The results clearly indicated the presence of copper iodide formed on copper with or without BTA. It seems that more than one complex can exist on the surface, with copper(I)-I-BTA being one and possibly copper(II)-BTA or copper(II)-I-BTA. The presence of Cu(I)-I-BTA complex was verified by the analysis, however the experimental results showed that in most cases the complex lead to acceleration of the corrosion rate. It was stated during the experiments that the addition of halides onto copper could accelerate indeed the corrosion but under certain conditions and concentrations could also be an effective inhibitor. The analysis of different BTA-KI films clearly demonstrated that the concentration of the solution and the solvent used affected the film formation.

6.12.6 XPS of BTA + PMT

6.12.6.1 PMT

The analysis of clean copper treated with 0.1M in ethanol showed that PMT formed a complex with copper I, which is found in atomic concentration 5.5at%. Oxygen had a strong peak at 531.9eV and it is also in relatively high concentration (12at%). The nitrogen peak was at 400.7eV and its atomic concentration was found to be 23.5at%. The peaks of sulphur are the ones that presented a peculiarity as there usually more than 2 peaks found. Sulphur content was found 10at%.

Copper I was also found on corroded copper treated with 0.1M PMT in ethanol. Copper (6at%), sulphur (9.2at%) and nitrogen (24.3at%) were found in similar concentration as

those of clean copper treated with the same solution. The oxygen content was lower in this case (6.3at%). The results of the analysis clearly indicate that PMT formed a complex with copper(I). Unlike previous treatments, here there were no cupric species detected.

6.12.6.2 BTA + PMT

The results of the analysis of clean coupon treated with 0.1M BTA + 0.1M PMT in ethanol showed mainly copper(I) (At% 7.4). Nitrogen was found 25at%, oxygen was at 5at% and sulphur 6.8at%.

Corroded copper treated with different BTA + PMT solutions showed a similar picture. Copper I was detected. The percentage of copper was found in the case of 0.1M BTA + 0.1M PMT in ethanol to be 4at%, the nitrogen 28at% and the sulphur 8at%. Oxygen was low (2at%) and interestingly chlorides were below detected limits (<1at%).

Of great interest is that BTA was mainly bonded to copper I in the case of PMT or mixtures of BTA + PMT. The way concentration affected the film formation was reflected in the different solutions. Only in treatments where higher BTA concentration (0.25M) was used in combination with 0.1M PMT in ethanol showed a weak copper II peak. Nitrogen content was slightly lower (24at%) and sulphur 5.3at%. Chlorides were also low. Oxygen was in similar levels as in the previous case. It seems that the concentration affected only slightly the film formation (see Appendix 6).

6.12.7 Elemental ratios

The atomic concentration ratios between certain elements can give valuable information about the film found on the surface. For example nitrogen and/or sulphur which are basic elements of most inhibitors tested are the elements bonded to copper. A general assumption is that the higher the ratio between nitrogen and/or sulphur to copper, the thicker the film formed on the surface. However the thickness alone is not indicative of the efficiency of a treatment. Another interesting aspect to look into is the ratio between oxygen and copper or chlorides and copper. Chlorides and oxygen have been reported to be incorporated into the copper-inhibitor films (e.g. KEX treatments). In case of BTA treatments high percentage of chlorides denote Cu(II)-BTA complex (Brostoff, 1997: 103).

Table 6.34 showing the atomic concentration ratio allows a comparative review between the different treatments. It is important to mention that the ratios between nitrogen to copper might not only be due to the high nitrogen content, but in some cases to very low copper. The first column shows the ratio between nitrogen and copper found on the surface, whilst the second column is also the ratio between nitrogen and copper, however here the overall nitrogen content is divided by the number of nitrogen atoms found in the inhibitor molecule. For example, treated copper with 0.01M AMT in water exhibited high N: Cu ratio (5.9) whilst the same ratio of the 0.01M AMT treatment in ethanol is a lot lower (1.7). The atomic concentration percentage of nitrogen is higher in the latter case as is the copper which is also significantly higher (3.9 and 15.8at% respectively). The combination of two compounds can undoubtedly result in different elemental ratios depending on the concentration and/or solvent used. The factors examined in the experimental part affect the

film formation and this is also demonstrated by the ratios. For example, on corroded copper the treatment of 0.25M BTA + 0.1M ETH in ethanol showed a high copper to nitrogen ratio and relatively low oxygen to copper and chloride to copper ratios. The same compounds in an equimolar solution (0.1M BTA + 0.1M ETH in ethanol) resulted in higher values of the examined ratios demonstrating the effect that concentration of the solution has.

The effect that the solvent has was demonstrated in the case of treatments of corroded copper with BTA + BZA. The same solutions (0.1M BTA + 0.1M BZA) in deionised water or ethanol resulted in different ratios. Although the nitrogen to copper ratio was higher in the case of an aqueous solution, the oxygen to copper and chloride to copper ratios were higher than in the case of ethanol. BTA + KEX treatments were also affected by the concentration and the solvent with ratios varying depending on the solution used. Interestingly the AMT and BTA + AMT treatments showed sulphur to copper ratios that were almost unvarying. The nitrogen to copper ratios changed depending on the treatment. The ratio increased with higher BTA concentration as expected.

6.12.8 Discussion on XPS results

The results of the analysis showed that all of the clean coupons were covered as expected with copper oxides. Copper is very reactive and it is very hard to obtain a copper surface free of corrosion. Therefore, it is more appropriate when discussing these experiments and analysis to keep in mind that the "clean" copper coupons were covered with thin air formed copper oxides (mainly copper I oxide) as indicated by the XPS results. The distinction between metallic copper and copper oxide is not possible without the Cu *LMM* Auger lines

(Briggs and Rivière, 1994:126). The value of the Cu *LMM* was indicative of copper I oxide not of metallic copper.

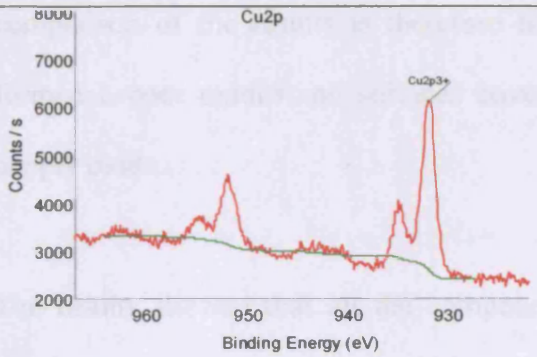


Fig a. BTA 0.25M + AMT 0.01M/EtOH, corroded copper

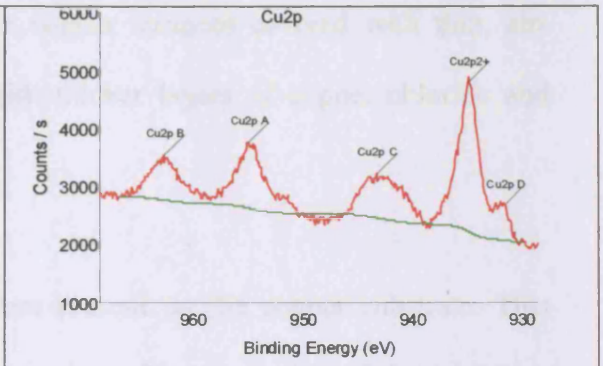


Fig. b. BTA 025M + 0.1 BZA/EtOH, corroded copper

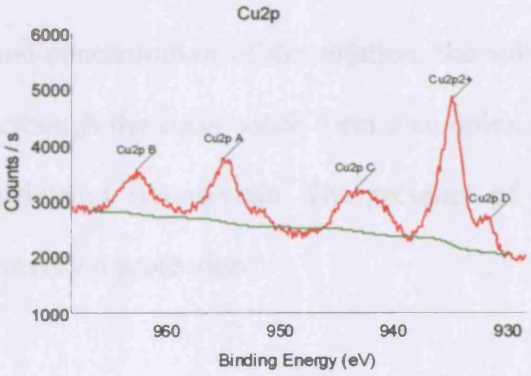


Fig. c. BTA 0.25M + ETH 0.1M, corroded copper

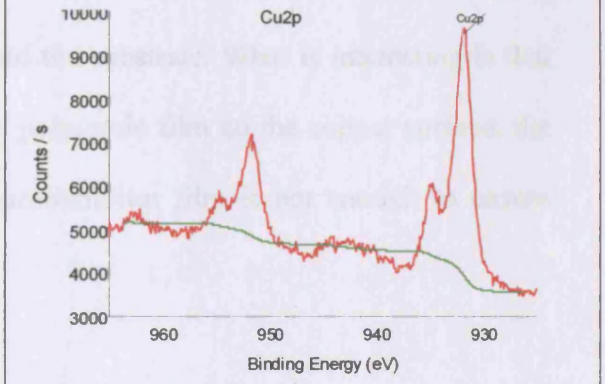


Fig. d. BTA 0.25M + 0.1M KI/EtOH, corroded copper

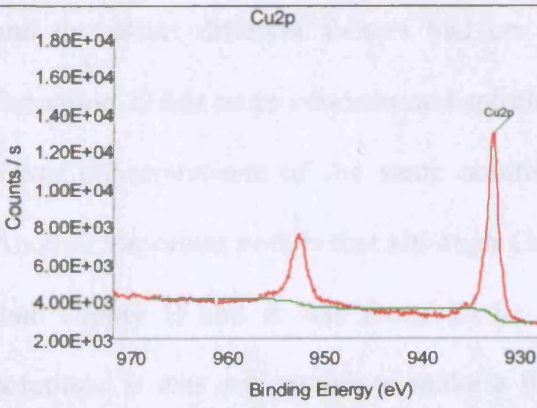


Fig. e. BTA 0.25M + KEX/EtOH, corroded copper

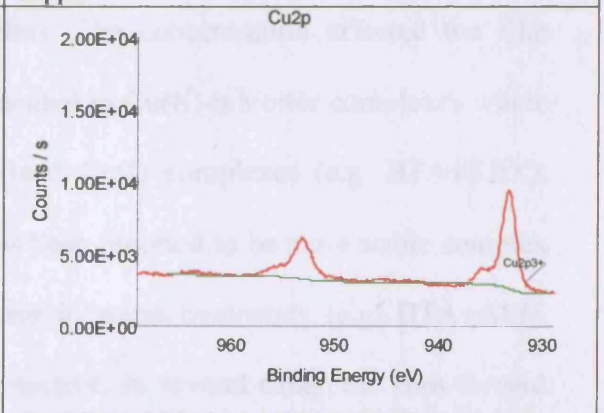


Fig f. BTA 0.25M + 0.1M PMT/EtOH, corroded copper

Figure 6-28. (a-f) Comparison of Cu2p XPS spectra for the same BTA solution (0.25M) and additives. Each combination of inhibitors created a different complex with either Cu(I) like a, d, e and f, or Cu(II) like b and c (BTA with BZA and ETH respectively).

The comparison between the clean and corroded copper coupons is still valid for various reasons. Firstly, archaeological and/or historical copper always has corrosion. The comparison of the results is therefore between copper surfaces covered with thin, air-formed copper oxides and surfaces covered with thicker layers of copper chloride and copper oxide.

The results showed that all the compounds were present on the copper substrate. This means that the compounds form a complex with copper. The adsorption of the inhibitors into the copper substrate varied depending on the chemical composition of the compound, and concentration of the solution, the solvent and the substrate. What is interesting is that although the compounds form a complex and/or polymeric film on the copper surface, the efficiency is uncertain. The presence of a copper-inhibitor film is not enough to ensure corrosion protection.

The XPS results gave valuable information about the chemical nature of the films formed and the effect different factors had on the films. The concentration affected the film formation. Often more concentrated solutions resulted in Cu(II)-inhibitor complexes where lower concentrations of the same solution formed Cu(I) complexes (e.g. BTA+KEX). Another important note is that although Cu(I) has been reported to be more stable complex than copper II and it was found to be the case in some treatments (e.g. BTA+AMT solutions) it was not enough to make a film protective. In several cases, the film formed was a Copper(I) complex (e.g. BTA+KI, BTA+KEX) but the results of the accelerated

corrosion tests showed these treatments were not effective and often caused acceleration of corrosion.

The oxygen peaks also provide substantial information in terms of the complexes. Certain complexes presented extremely high oxygen content. ETH and KEX molecules include oxygen however high oxygen concentrations were found even in coupons treated with KI or BZA. Nevertheless, the mixture of these compounds with BTA resulted in low oxygen levels.

The presence of oxygen might be the result of a number of reasons. The formation of a porous, oxygen permeable film is one of them as is the formation of a complex incorporating also oxygen in its structure. Most of the treatments with high oxygen concentration were not effective. AMT was an exception to this.

Another element important for the analysis was chloride. Chloride on the pre-corroded copper coupons was in the form of nantokite found underneath cuprite. The treatment of the coupons with inhibitors caused a significant drop in the chloride concentration and in some cases it was below the detection limits of the technique. In general chloride levels were lower than the levels of the untreated coupons and in some cases it was below detection limits however there were treatments where the concentration was high (e.g. ETH treatment). The atomic concentration percentages of oxygen and chloride seemed to increase in aqueous solutions.

Nitrogen and sulphur were of paramount importance as the compounds form a complex with copper through them. The concentrations of nitrogen and sulphur also varied depending on the solutions. In case of BTA and AMT combination, the amount of N and S changed depending on the concentration and solvent of the solution. The most effective treatment according to the experimental weight change data was that of 0.1M BTA + 0.01M AMT in ethanol, the analysis of which showed high levels of both N and S. Although in all BTA + AMT treatments nitrogen concentration was high, this solution was the one that presented higher S levels than all of the other solutions of the same combination.

The treatments presented significant differentiations regarding their complexing with copper(I) or copper(II) which were greatly affected by the copper substrate. Both clean and corroded copper were covered with both copper oxides, with copper(I) oxide (cuprite) being predominant. The results of BTA treatments showed that inhibition could cause changes on the copper surfaces, verified also in this chapter. For example, KI on clean and corroded copper formed complexes with copper(I), when mixed with BTA it formed complexes with both however on clean copper, copper(II) was predominant and on corroded copper they formed complexes with copper(I). An interesting point, however, is that the BTA complex with copper is changed when other compounds are added into the solutions. In most cases, copper(I) was found to be the predominant complex of BTA with AMT, KI, KEX and PMT and copper(II) in the case of BTA mixed with amines such as BZA and ETH.

6.13 Discussion of results

The analytical FTIR and XPS findings allowed a better understanding of the inhibition processes between BTA and the additives. The combination of BTA with AMT proved to be the only one exhibiting a synergistic effect in all tested solutions. The factors affecting BTA such as time of immersion, concentration and solvent did not seem to affect the efficiency. More importantly it was proven to be effective on the test coupons at very low concentrations. The fact that the combination worked is also explained by the analysis of the surface film. The results showed there are probably two complexes coexisting, a Cu-AMT and a Cu-BTA. The presence of AMT into the BTA solutions affected even the Cu-BTA complex. BTA bonded mainly to Copper(II) when used alone, whilst in case of BTA+AMT treatments, there are mainly cuprous complexes: Cu(I)-BTA and Cu(I)-AMT. There seems to be immediate reaction between the inhibitors and copper leading to the formation of a very stable complex/polymeric film. The predominant complexes were Copper(I), generally accepted as more stable than Copper(II). This is the reason, factors such as concentration of the solution, solvent, and time of immersion, did not have a great effect on the overall process. The atomic concentrations of the treatments showed that nitrogen is always high in content, whilst the percentage of sulphur fluctuates. The higher sulphur content was found in the coupons treated with the 0.1M BTA + 0.01M AMT which was found to be the most effective of the combination.

The two amines (BZA and ETH) examined aimed at adjusting the pH levels to more neutral levels as well as affecting the kinetics of the polymeric film. It was proven that the addition of these amines into BTA, instead of improving the overall efficiency, caused acceleration

of the corrosion rate. The analysis showed that the film formation was affected by many factors. The effect on the kinetics of the film growth was not proven with the techniques used and it was out of the scope of this research, however, there was no doubt that the films were porous and oxygen permeable as it is understood by the XPS results. The latter might be the reasons the films were not effective.

The addition of KI presents particular interest. Halides (I, F, Cl, Br) added to a metal/ inhibitor system enhance the adsorption of the organic molecules. KI has been examined for its synergism with a number of inhibitors and different metals (copper, steel, aluminium, zinc). The results of the experiments were contradictory. In general KI was not found effective in increasing inhibition. There was one solution that exhibited higher inhibitive efficiency than BTA alone, and that was 0.1M BTA + 0.01M KI in deionised water. It is evident from the FTIR results that there was CuI (copper iodide) formed, probably the complex formed was a Cu-I-BTA. The predominant complex is that of Cu(I)-I-BTA with some Cu(II)-I-BTA also formed. The amount of iodide found varied greatly with corroded copper bearing more than clean copper. The variation in the efficiency and the analytical results indicate that the film formed is dependent on the concentration, the time of immersion and the solvent. Additionally there is no complete coverage of the surface with the complex, which can lead to accelerated corrosion. Some of the colour alterations imposed on both the clean and corroded copper coupons make it unacceptable at this stage for further testing on archaeological objects.

The treatment of BTA + KEX was also unsuccessful. The combinations did not increase the inhibitive efficiency of BTA. On the contrary, most of the BTA + KEX solutions caused acceleration of corrosion. There was evidence of two polymeric films on the surface (see FTIR and XPS results) however, the film formed on the surface lacked coherence with the substrate. Also the colour changes were above the acceptable levels of colour changes for archaeological objects and it was decided not to continue the testing on real objects.

PMT is an inhibitor that exhibited moderate efficiency alone or in combination with BTA. It did not cause a significant increase in the BTA efficiency, in fact in some cases the efficiency was lower that that of BTA, however it did not cause acceleration of corrosion either. The combination did not cause colour changes in the treated coupons and also had an effect in the Cu-BTA formation as it was found to be Cu(I)-BTA not Cu(II)-BTA as was the case in most of the BTA solutions.

Based on these results, it was decided to apply solutions of the combination of BTA with AMT on selected archaeological copper alloy artefacts for comparison to the tests on pre-corroded copper coupons. Apart from the obvious reasons for selecting this combination, the combination of BTA with PMT was also selected, as it was found a "safe" combination. It did not cause colour alterations on the surface and also, even if synergism with BTA was not proven, it was an inhibitor that was quite effective on its own. It was also considered necessary to test one more combination for comparative reasons. The testing on archaeological objects and the results are described in the following chapter.

CHAPTER 7

7 Testing of selected treatments on Excavated Copper Alloy Artefacts

7.1 Introduction

The efficiency and mode of action of certain inhibitors and combination of inhibitors on clean and artificially corroded copper coupons was examined in the previous chapters. The experimental and analytical results contributed to a better understanding of the inhibition process and the way that certain variables, usually unconsidered by archaeological conservators, affect the inhibitive efficiency. The efficiency of inhibitors on coupons containing nantokite is of great importance in conservation. Nantokite is very reactive and in contact with oxygen and humidity from the environment will react to form atacamite and/or paratacamite accelerating the corrosion process. The evaluation of these compounds on artificially corroded copper coupons allowed a direct and reliable comparison of the efficiency, within limits, of different inhibitor solutions whilst decreasing recognised margin of errors.

Chapter 5 discussed BTA and examined the way selected variables affect the film formation and subsequently its efficiency. The application method was found to have a significant effect in the overall process, by affecting the chemical nature and properties of

the copper-BTA polymeric film formed on the surface, which in turn affects the effectiveness of the treatment.

Chapter 6 evaluated six compounds as potential corrosion inhibitors alone or in combination with BTA, making use of the synergistic effect reported for some of them in the literature. The results showed that the combination BTA + AMT clearly exhibits synergistic effect with improved inhibitive efficiency. The results were very promising for use on archaeological objects as apart from being an effective inhibitor the BTA + AMT combination did not cause any significant alteration on the appearance of the coupons.

Having tested these inhibitors on coupons in combination with the analytical results, one could draw conclusions about their mode of action. The rationale of all the accelerated corrosion testing as well as the restrictions and limitations they entail were developed in chapter 4. However, no laboratory testing could be entirely valid without field trials. There are no laboratory tests that could completely represent the effect new compounds would have on real objects. Due to the complexity of corrosion products and layers found on archaeological objects it was necessary to do some further testing of the most successful inhibition treatments on real copper alloy objects.

To assess the laboratory results, testing on real objects was performed. The aim of the testing on excavated copper alloy artefacts was to examine some of the tested treatments found effective during the laboratory testing to examine or not their efficiency when treating real archaeological objects in real field conditions.

Corrosion of archaeological metal artefacts is rarely uniform and treatment evaluation based on weight change measurements was not deemed valid due to the variety in composition of copper alloys and corrosion products. To assess the effect of the treatments taking place on archaeological artefacts, a scale was created taking into account the bronze disease outbreaks found on the objects after the exposure to high relative humidity. This way one could objectify the process.

7.2 Objects used for field tests

The testing on real objects was performed on objects coming from two different archaeological sites. Kaman Kalehöyük is an excavation located in a rural area in Central Anatolia in Turkey whilst Mochlos is a coastal site in east Crete, Greece. The burial environmental conditions of the two sites are very different, even so both are rich in copper alloy finds which suffer with chloride-containing active corrosion. Even though the aim in both cases was to apply inhibitor treatments and monitor them over a span of years, the objectives were quite different. Testing in Kaman Kalehöyük was very rigorous and was based on the application of the treatments on a large number of small finds (220 objects were treated in total). The Mochlos testing focused on very selective testing of larger dimension objects. Each test is discussed separately.

7.2.1 Kaman Kalehöyük

The main bulk of these tests were carried out in Kaman Kalehöyük in Turkey. The site Kaman Kalehöyük has brought to light a significant number of copper alloy objects dating

from the early Bronze Age to the Ottoman period. The objects selected were all bronzes, some of which had high lead content as verified by the X-ray Fluorescence analysis of a small selection of five objects done by S.Yamada in 2000. The non-destructive XRF surface analysis was used only as an indication of the metals present in the alloy artefacts as this was surface analysis of the corroded surface.

The alkaline soil conditions of the site resulted in poor preservation of metal objects. A pH analysis of soil samples taken from the site had been measured to be between 8.0 and 9.3. Twilley (1996) analysed six bronze fibulae using XRD and FTIR and found that the burial environment affects the formation of the corrosion products more than the composition of the alloy (Twilley, 1996: 239). The corrosion products found by Twilley were tenorite (CuO), cuprite (Cu_2O) and cassiterite (SnO_2). However, most of the copper alloy objects excavated from the site suffered with bronze disease.

The excavation had unearthed a large number of small finds, a lot of them of minor aesthetic and/or archaeological value as they were scrap pieces, nails, fragments, etc. None of the important pieces were selected for the testing. The selection of the objects to be tested was based on their degree of corrosion after communication with Dr. S. Omura, director of the site and Dr. M. Omura, responsible for the objects. The copper and copper alloy objects selected had been excavated in recent years (most of them were excavated the year of the treatment whilst others were excavated in previous excavation seasons) and come from the full range of different archaeological periods found in Kaman Kalehöyük. The excavation houses a well organised conservation laboratory which deals foremost with

copper alloy artefacts. The laboratory was run for many years by Dr. G. Wharton, director of conservation of the site and there are well established protocol treatments for the objects. Only the objects suffering with active corrosion are usually treated with BTA, whilst the others were cleaned to remove soil deposits and stored in silica-containing air-tight plastic boxes.

7.2.1.1 Methodology

The objects were mechanically cleaned to reveal the original shape (as much as was permitted by the corrosion) and degreased in an acetone bath for an hour following the treatment protocol of the site. Following this, the objects were classified into three groups, depending on the degree of corrosion. This classification was based on visual examination under a stereomicroscope, a relatively subjective procedure. The first group was for objects in a relatively good condition with metal core present underneath the corrosion layers. The second group included more corroded objects that also had metal core left, whilst the last group included heavily corroded objects most of which were totally mineralised, but which still had active corrosion.

The grouping of the objects was carried out in collaboration with the other conservators of the site. Different conservators were given identical directions in assigning the levels and were asked to classify the objects into the three main groups. The objects that were not confidently classified into a group were excluded to eliminate errors.

Weight-change measurements are only valid when dealing with uniform corrosion therefore, were not applicable in this case. Corrosion is directly related to the metal and/or

alloy composition, the size and the shape of the object, the environment to which the object has been exposed to as well as post excavation changes. The objects used presented great diversity in terms of date, composition of metal alloy and corrosion. In order to moderate error due to this diversity, batches of ten objects were used for each treatment. This number of objects per group is considered adequate statistically (Brazil, 1999). The objects for each treatment set included a selection from each of the various corrosion groups in order to have a range of object types, however, to eliminate systematic errors during the selection these were randomly chosen from within each group. The total number of objects used was 220.

The treatment testing and evaluation occurred during the excavation periods of 2000 and 2001 (July-August). Similarly to the laboratory experiments, different factors were examined. The main treatments tested were those of BTA, BTA+AMT and BTA+PMT in different concentrations, solvents and application methods. The tested treatments, the factors examined and colour change observations are shown in Table 7.1.

In the first set of tests carried out during the excavation season of 2000 the inhibitors were applied following the treatment protocol used in the conservation laboratory. The objects were immersed into the inhibitor solution for 3 hours under vacuum (40cmHg). This method was established by G.Wharton, director of conservation of Kaman Kalehöyük excavation (G.Wharton, personal communication, 2000).

Table 7.1. Kaman Kalehoyuk testing was carried out on 220 objects divided into batches of 10. Each group assessed a different treatment.

Group	Treatment/inhibitor solution	Factors examined	Colour changes
I	BTA 0.1M/EtOH	Application, concentration, solvent	No colour changes
II	BTA 0.1M/H_2O	Application, concentration, solvent	No colour changes
III	BTA 0.25M/EtOH	Application, concentration, solvent	Slight darkening, BTA crystals formation
IV	AMT 0.01M/EtOH	AMT, solvent	Spots of yellow precipitate on top of nantokite
V	PMT 0.1M/EtOH	PMT	Whitish precipitate
VI	BTA 0.1M + AMT 0.01M/EtOH	Application, concentration, solvent, AMT	Some yellow spots
VII	BTA 0.1M + AMT 0.01M/ H_2O	Application, concentration, solvent, AMT	Some yellow spots
VIII	BTA 0.25M + AMT 0.01M/EtOH	Application, BTA concentration, AMT	Some yellow spots
IX	BTA 0.1M + PMT 0.1M/EtOH	Application, BTA concentration, PMT	Whitish precipitate
X	BTA 0.25M + PMT 0.1M/EtOH	Application, BTA concentration, PMT	Whitish precipitate
XI	CONTROLS	2000	
XII	CONTROLS	2001	
XIII	BTA 0.1M/ H_2O	Application, BTA concentration, solvent, time of immersion	No colour changes
XIV	BTA 0.1M/EtOH	Concentration, time of immersion, solvent	No colour changes
XV	AMT 0.01M/ EtOH	Application, solvent	Some yellow spots
XVI	BTA 0.25M + AMT 0.01M/EtOH	Application, BTA concentration, AMT	Some yellow spots
XVII	BTA 0.1M + AMT 0.01M/EtOH	Application, BTA concentration, AMT	Some yellow spots
XVIII	BTA 0.1M + AMT 0.01M/ H_2O	Application, BTA concentration, AMT	Some yellow spots
XIX	BTA 0.01M + AMT 0.01M/ EtOH	Application, BTA concentration, solvent, AMT	Some yellow spots
XX	BTA 0.01M + AMT 0.01M/ H_2O	Application, BTA concentration, solvent, AMT	Some yellow spots
XXI	BTA 0.25M-1	Application, BTA concentration	Slight darkening
XXII	BTA 0.25M- used solution	Application, BTA concentration	Slight darkening, formation of white BTA crystals and tidelines

Following the results of the first set, the second set of tests was carried out the following year (2001) changing the application methodology, the coupons were simply immersed into the solutions for an hour. This change allowed testing of the application method as an additional factor affecting the efficiency. In this way, direct comparisons of the field tests with the laboratory tests were feasible.

All of the treated objects were left in polythene boxes the conservation lab without protective coating and are being monitored on a regular basis. Only long term monitoring can confirm the final efficiency of the treatments.

7.2.1.2 Treatment selection

The choice of treatments to be tested was based on the results of the accelerated corrosion testing. Different BTA treatments were assessed based on the results of chapter 5 and two combinations tested in chapter 6. The combinations tested were those of BTA+AMT and BTA+PMT. The results of the analysis showed that all the BTA+AMT treatments were effective because of the synergistic effect between the two compounds. The second combination was tested because, although not as effective as the previous one, it had shown that it could be potentially effective under certain conditions. It is worth mentioning that the choice of inhibitors was such as to run no risk of accelerating the corrosion rate. Combinations that were found to accelerate the corrosion rate were immediately rejected as well as treatments that were causing significant colour alterations (see table 7.1). The solvent used for the solutions were pure ethanol (95%) and deionised water.

7.2.1.3 Evaluation of treatments

The efficiency of the treatments was tested against high RH in a twenty-four hour exposure to almost 100% RH. This is a method used by some conservators to check whether the BTA treatment has been successful or not but it does represent a risk to the objects which is limited by close monitoring. The humidity chambers were created using plastic containers with small water containers for humidity, the objects were exposed to the damp environment by suspending them in plastic netting within these boxes. All the groups were exposed simultaneously to avoid bias caused by variations in temperature, an uncontrollable factor under those conditions. Unfortunately, the excavation season, and subsequently the testing of the inhibitors, was held during the summer months and the

boxes were subjected to a high temperature (temperature during the day of the tests reached 40°C). Because of the high temperature, there was condensation in the boxes within the first hour. The test was proven to be quite severe as the temperature in combination with the high RH accelerated corrosion. The validity of these tests lies in the comparison between the objects within a group and between different groups. Apart from the treated objects, a group of ten untreated objects were exposed to the same conditions.

Figure 7.1. The object exhibited extensive corrosion after the exposure to high RH and was rated as IV.

Following the twentyfour-hour exposure, the objects were allowed to dry and their state of conservation was recorded in the four level scale based on the extent of corrosion observed on the objects (see chapter 4). The evaluation of the treatments was based on visual assessment of new active corrosion outbreaks observed under the stereomicroscope. The assessment was carried out by different conservators. Although classification of corrosion to levels I and IV were fairly easy, there was occasionally confusion between levels II and III. Any problems regarding classification were sorted out at the end of the exercise where all the groups were spread for the final assessment with participation of all the conservators involved. Also, to avoid favouring of a treatment, all the treatments were coded, so that no one (not even the author) would know which group represents which treatment.

All of the objects were photographed and documented in a database made purposely in File Maker Pro. The fields included the object number, the year of the excavation, brief description and condition assessment of the object, cleaning and treatment procedures followed, inhibitor group, comments on colour changes after the treatment and after exposure to RH and finally assessment and score of the object. The database helped in the comparative assessment of the treatments and also any queries related to the behaviour of an object could be linked to many different aspects such as the year the object was excavated, whether there was active corrosion observed before the treatment or not, etc.

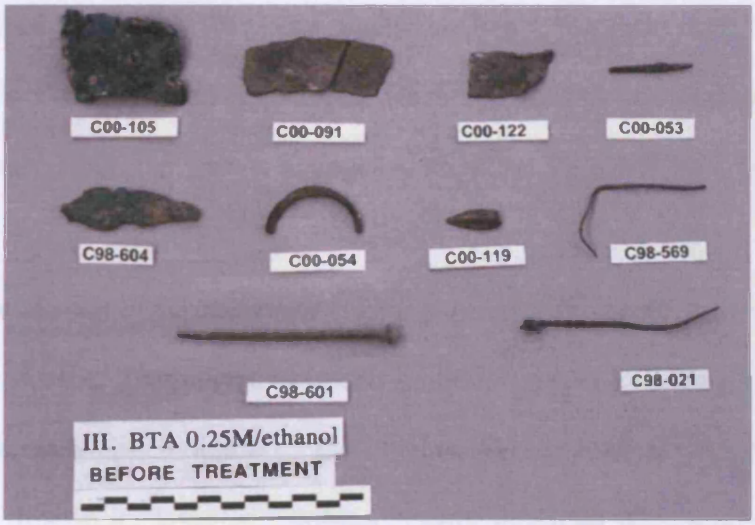


Figure 7.2.Group III was treated with 0.25M BTA in ethanol.

7.2.1.4 Colour changes

Colour changes caused by the treatments were assessed by visual examination. BTA treatments caused slight darkening of the corroded coupons. The darkening was less obvious on the objects compared to the coupons. Objects treated with 0.1M BTA in ethanol or water did not present any significant changes. Objects treated with more concentrated

solutions (i.e. 0.25M BTA in ethanol) appeared slightly darker. The formation of BTA crystals on the surface of the objects upon drying was a common observation, however, this was observed only on some of the objects treated with 0.25M BTA in ethanol. The BTA crystal formations along with white precipitate tidelines were more evident on objects treated with re-used solution of 0.25M in ethanol.

Some of the objects treated with 0.01M AMT in ethanol showed the formation of yellow precipitate spots on top of exposed nantokite. The precipitate was easily removed using a cotton swab soaked in ethanol. The same precipitate to a lesser extent was found on objects treated with BTA + AMT treatments. Except for the occasional formation of the precipitate there were no other significant colour changes in all of the BTA + AMT treatments.

The objects treated with PMT and BTA + PMT solutions presented some colour changes. Although coupons treated with these solutions in the laboratory experiments did not present significant colour changes, in some of the objects, objects treated with 0.1M PMT were covered with a thin white layer of inhibitor, easily removed with solvents. The objects treated with the two BTA + PMT solutions presented white spots with inhibitor residues also easily removable with ethanol. As it turned out, all the changes were related to the formation of a superficial layer that was removed with the use of cotton swabs soaked in ethanol.

The difference in colour changes between the coupons and the objects was expected and are related to the fact that the surface of the coupons was covered with cuprite whilst the

objects were covered with a variety of corrosion products, including copper oxides, copper carbonates, and copper chloride (exposed nantokite during cleaning). Visual assessment of colour changes is a subjective matter. The main difference with the laboratory tests was the formation of white precipitate on objects treated with PMT and BTA + PMT solutions and the yellow spots on AMT, BTA + AMT treatments. The formation of yellowish spots has been also observed by others (see chapter 3). Tidelines on contact points between the objects and the net they were placed on to dry were also observed but not taken into account as this was considered merely due to the procedure followed, not the treatment applied.

7.2.1.5 Results

7.2.1.5.1 Results of test set 1 (2000)

As mentioned earlier, the treatments in this set of tests were applied using the protocol of the lab, 3 hours of immersion under vacuum. The evaluation of the first tests showed that 0.1M BTA + 0.01M AMT in ethanol was by far the most effective treatment. None of the objects treated exhibited any signs of new corrosion. The same in water was the second best treatment, followed by 0.25M BTA + 0.01M AMT in ethanol. The combination 0.1M BTA + 0.1M PMT in ethanol was the next most effective, followed by 0.25M BTA in ethanol, 0.25M BTA + 0.1M PMT in ethanol, 0.1M BTA in ethanol, 0.1M BTA in deionised water, 0.1M PMT in ethanol, 0.01M AMT in ethanol and finally the controls. These results were, in general terms, in agreement with the laboratory results, with some interesting exceptions (see table 7.2).

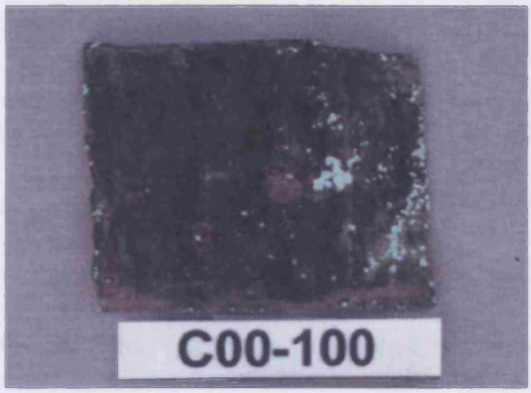


Figure 7.3. Object C00-100, treated with 0.01M AMT/EtOH (Group IV) after exposure to high RH. The object presented extensive pitting corrosion and was ranked as IV.

In terms of BTA treatments the ranking of effectiveness followed that of the laboratory tests, with 0.25M in ethanol being the most effective. Contrary to this, AMT was found an effective inhibitor when applied on pre-corroded coupons in the laboratory tests and in some cases even more effective than BTA alone. In these tests, AMT was found ineffective as all of the objects treated with AMT presented active corrosion. Its score, as will be discussed later on, was very close to that of untreated objects. All of the BTA+AMT treatments were found to be effective with 0.1M BTA + 0.01M AMT in ethanol showing no signs of active corrosion whatsoever. The ranking of the treatments changed slightly. The treatments of 0.25M BTA + 0.01M BTA in ethanol and 0.1M BTA+ 0.01M AMT in water were also close in effectiveness in the laboratory tests. In the laboratory tests 0.1M BTA + 0.1M PMT in ethanol was far less effective than 0.25M BTA, a reversal of the results obtained in these tests. Still, the differences were not that considerable.

7.2.1.5.2 Results of field test 2 (2001)

Based on the results of the field tests of the first set, the testing of inhibitive compounds the second year continued using only BTA, AMT and BTA + AMT treatments. PMT and BTA + PMT were rejected not only because of the effectiveness but mainly because of the colour changes they caused to the objects. The main difference between the two sets was in the application methodology. In the second field test, the objects were simply immersed into the solutions for an hour. This allowed the assessment of more factors affecting these treatments (see table 7.2).

The results of the second tests also showed 0.25M in ethanol being the most effective treatment with 0.1M BTA + 0.01M AMT in water and 0.01M BTA and 0.01M AMT in ethanol a close second. Following on from these treatments in order of effectiveness were: 0.1M BTA + 0.01M AMT in ethanol, then 0.1M BTA in ethanol, 0.25M BTA + 0.01M BTA in ethanol, 0.01M BTA + 0.01M AMT in water, 0.25M BTA in ethanol (re-used solution), 0.01M AMT in ethanol and finally 0.1M BTA in water (table 7.2).

One of the first things observed was the way the inhibitive efficiency changed in relation to the concentration of the solutions used. Surprisingly, the effective order of BTA + AMT treatments did not depend on the BTA concentration. Even low concentration solutions of the combination were as effective if not more effective as the more concentrated ones.

Another important point, looking at the two sets of field tests was that apart from two solutions (0.1BTA + 0.01M AMT in ethanol and water) that were the most successful

solutions in both cases, the ranking of efficiency changes, indicating that the duration of immersion affects the efficiency of a treatment. Although the treatments were applied under vacuum the first year its effect appeared to be minimal and evident only in the number of objects showing active corrosion in the two successful treatments. The effect of the duration of immersion is far greater indicating the significance it has on the efficiency of a treatment.

However the biggest surprise is the way that the BTA efficiency dropped in the case of treatment with an already used 0.25M solution, this is discussed in the next section.

7.2.1.5.3 BTA treatments

The most effective of the BTA treatments was found to be that of 0.25M in ethanol applied by simple immersion for one hour. In both groups treated with 0.1M BTA in ethanol and water for three hours under vacuum (field test 1), nine out of ten objects showed new active corrosion outbreaks. The objects treated with BTA 0.1M in ethanol were found in an overall better state than those treated with the same inhibitor dissolved in de-ionised water, in agreement with the laboratory results. However, although the solvent did affect the efficiency of BTA, with ethanol being a better solvent than deionised water, the difference in the results was marginal. The comparison between the two previous treatments with that of 0.25M BTA in ethanol showed that the latter is more effective, indicating that efficiency increases with concentration.

The comparison of treatments applied by simple immersion of the object into the solution for an hour (field test 2) showed that nine out of ten objects treated with the aqueous solution presented new outbreaks of active corrosion versus seven out of ten objects that were found to have active corrosion signs in the case ethanol where was used as a solvent. It seems that the solvent plays a more significant role especially in combination with the time of immersion.

The comparison between 0.1M BTA and 0.25M BTA solutions in ethanol applied by simple immersion was similar to the ranking observed in objects treated with the same solutions for three hours under vacuum. However, it is worth mentioning that the overall corrosion protection was increased in case where shorter periods of immersion were used. More specifically, the number of objects presenting corrosion was seven out of ten (for both treatments applied for an hour) versus nine out of ten observed in longer period of immersion, as it can be seen in table 7.2.

The application methodology did not affect, however, the 0.1M BTA in deionised water treatments as the results were similar. It appeared that for aqueous solutions this difference in the duration of immersion was totally insignificant. Although the two groups had the same overall score in the scale of efficiency, there were differences in the two groups which were related to the distribution of the corroded coupons into the different corrosion levels. The corrosion was more evenly distributed across the scale in the group immersed for three hours under vacuum. In the laboratory tests the time of immersion played the most significant role for aqueous solutions where twenty four-hour immersion resulted in actual

acceleration of corrosion. The difference between one and three hours was obviously of less importance and cannot be compared to that of twenty four hours. Apart from this, the effect of the factors in the field tests was in agreement with that of the laboratory tests.

The protection provided by 0.25M BTA in ethanol after 3-hour impregnation under vacuum was less than that provided after one hour of immersion. This difference is most probably related only to the length of time of immersion and not the application of the solution under vacuum. In theory the use of vacuum should facilitate the impregnation of the object by the inhibitor and help the inhibitor reach the metal core (if there is metal core left) that could enhance the effectiveness of the treatment. Therefore, in agreement with the accelerated corrosion testing results, the duration of immersion has a significant effect on the efficiency of a treatment.

The re-use of the BTA solution decreased significantly the corrosion protection provided by BTA. The solution tested was that commonly used in conservation practice, 0.25M in ethanol (approximately 3% w/v). The solution had been used earlier for the treatment of other objects, which stayed immersed in the solution for an hour. After exposure to high RH, seven out of ten objects from the group treated with freshly prepared BTA solution presented new corrosion signs. From those six, had minimal bronze disease spots (level I-visible under stereomicroscope). In the case of objects treated with re-used BTA solution, nine out of ten objects treated had more active corrosion. The tests with 0.25M treatments showed that the treatment was more effective when applied for an hour using freshly prepared solution.

7.2.1.5.4 BTA + AMT treatments

As has been mentioned in the discussion of the results of field tests 1 and 2, most of the BTA + AMT treatments were successful. Of great interest is the fact the there was only one group that did no present any signs of new corrosion and that was of 0.1M BTA + 0.01M AMT in ethanol impregnated under vacuum. It is also important to note that the treatments with the same concentration dissolved in deionised water were also very effective with only four out of ten objects exhibiting minor spots of renewed corrosion. Of interest here is that the lower concentration solutions (0.01M BTA + 0.01M AMT) were also found in comparison with other treatments quite successful in the treatment of archaeological objects. These treatments seem to be dependent to a much lesser extent to the factors that proved to be of major significance for BTA. An observation of this is that although more concentrated BTA solutions provide better protection, in the case of the use of BTA in combination with AMT, it is not the more concentrated solution that was found to be the more successful. Another factor that was also found to be interesting in this set of field tests was the solvent used, which was also of little significance in this combination.

The synergistic effect between BTA and AMT was demonstrated in the laboratory experiments and these results also confirm its existence. The results are generally in agreement with those of experiments BTA+AMT 1, 2 and 3 of chapter 6.

Table 7.2. The evaluation of the treatments of the Kaman Kalehoyuk testing was based on the number of objects with BD as well as its extent.

Group	Treatment/inhibitor solution	0	I	II	III	IV	Total objects with BD	No of objects	Score	Average Score	Comparison with untreated	StDev
I	BTA 0.1M/EtOH	1	1	3	4	1	9	10	**23**	2.30	0.60	1.16
II	BTA 0.1M/H2O	1	1	3	3	2	9	10	**24**	2.40	0.50	1.26
III	BTA 0.25M/EtOH	1	1	6	2		9	10	**19**	1.90	1.00	0.88
IV	AMT 0.01M/EtOH	0	1	2	3	3	9	9	**26**	2.89	0.01	1.05
V	PMT 0.1M/EtOH	0	1	4	3	2	10	10	**26**	2.60	0.30	0.97
VI	BTA 0.1M + AMT 0.01M/EtOH	10	0	0	0	0	0	10	**0**	0.00	2.90	0.00
VII	BTA 0.1M + AMT 0.01M/ H2O	6	2	2			4	10	**6**	0.60	2.30	0.84
VIII	BTA 0.25M + AMT 0.01M/EtOH	3	5	2			7	10	**9**	0.90	2.00	0.74
IX	BTA 0.1M + PMT 0.1M/EtOH	2	3	3	1	1	8	10	**16**	1.60	1.30	1.26
X	BTA 0.25M + PMT 0.1M/EtOH	1	3	4		2	9	10	**19**	1.90	1.00	1.29
XI	CONTROLS	2			3	5	8	10	**29**	2.90		1.60
XII	CONTROLS	0	2	3	1	4	10	10	**27**	2.70		1.25
XIII	BTA 0.1M/ H2O	1	3		3	3	9	10	**24**	2.40	0.30	1.51
XIV	BTA 0.1M/EtOH	3	2		5		7	10	**17**	1.70	1.00	1.91
XV	AMT 0.01M/ EtOH	1		5	1	2	8	9	**21**	2.33	0.37	1.22
XVI	BTA 0.25M + AMT 0.01M/EtOH	1	3	4	3		9	10	**20**	2.00	0.70	0.82
XVII	BTA 0.1M + AMT 0.01M/EtOH	3	2	3	1	1	7	10	**15**	1.50	1.20	1.35
XVIII	BTA 0.1M + AMT 0.01M/ H2O	4	2	2	2		6	10	**12**	1.20	1.50	1.22
XIX	BTA 0.01M + AMT 0.01M/ EtOH	1	5	4			9	10	**13**	1.30	1.40	0.67
XX	BTA 0.01M + AMT 0.01M/ H2O	1	2	2	3	2	9	10	**23**	2.30	0.40	1.34
XXI	BTA 0.25M-1	3	6	1			7	10	**8**	0.80	1.90	0.63
XXII	BTA 0.25M- used solution	1	1	3	4	1	9	10	**23**	2.30	0.40	1.16

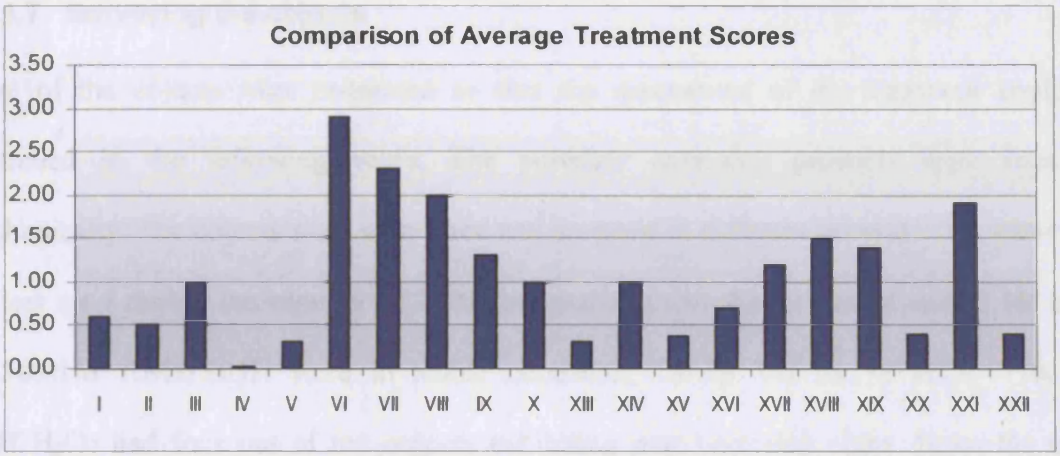
7.2.1.5.5 BTA + PMT treatments

The effectiveness of the BTA + PMT combination was found to be more successful than expected based on the laboratory tests. The 0.1M BTA + 0.1M PMT was found to be more effective than 0.25M BTA + 0.1M PMT both in ethanol. In the former solution, since the effectiveness of the combination was higher than that of 0.1M BTA in ethanol and 0.1M

PMT in ethanol, there seems to be synergistic effect between the two compounds. An assumption about the formation of the whitish precipitate that was not observed in the laboratory is that it might be due to the 5% water contained in the ethanol used (ethanol used in lab experiments was of analar grade 99%).

7.2.1.6 Comparative study of treatments using CARS scale

The scale created for the assessment of the treatments took into account not only the number of objects presenting active corrosion signs after the exposure to high RH, but also the extent of corrosion observed on them. The scale had five levels of different degrees of corrosion and each of the levels had a score for the assessment. After the classification of the objects of a group into the corrosion levels, the total score of corrosion was calculated by summing the number of objects of each level multiplied by the score of the level (see table 7.2). Each group had a number representing its effectiveness. Level 0 represents the number of objects without any corrosion. The smaller the number is the higher the effectiveness of the treatment. In this case, the objects of group VI (0.1M BTA + 0.01M AMT in ethanol) where none of them had new corrosion scored 0 (10 objects at 0 level) whilst the group of control coupons that had 3 objects at level III and five objects at level IV scored 29. In order to compare the treatments it was necessary to calculate the average score for the group by dividing the score with the total number objects the group had. The average score was subtracted from the average score of the control group. The final number explained the efficiency in comparison with the untreated groups. In this case, the higher the number the more effective the treatment (C.Orton, personal communication, 2006).



Graph 1. Graphic representation of relative effectiveness of the treatments in relation to the untreated objects of each year. The most effective treatment was of group VI, 0.1M BTA + 0.01M AMT/EtOH which has the highest score in the graph.

Table 7.2 shows the groups of inhibitors, the corrosion classification of the group objects, as well as the number of objects having new corrosion for each group, the total number of objects of the group, the score and average score and the score after its subtraction from the control number. The Standard Deviation (StDev) of each treatment is also shown in the last column of the table. The number used as control was for 2000 the score of XI untreated group and for 2001 the score of XII untreated group. These values are also presented graphically in graph 1.

The score number is just a representation of the results. It is not an actual value and it cannot be converted to efficiency percentages. This is a relative scale and its validity and strength is that the testing was carried out under the same conditions with caution to reduce human errors and favouring of a treatment. The only treatment that one can positively say was 100% effective would be that when none of the objects presented any corrosion.

7.2.1.7 Surveying the objects

None of the objects were re-treated so that the assessment of the treatment could be continued in the following years. The powdery corrosion products were removed mechanically. The objects were monitored and assessed in different intervals. The survey of the test set 1 during the summer of 2001 revealed that the objects treated with 0.1M BTA and 0.01M AMT/EtOH were in stable condition. Group VII (0.1M BTA + 0.01M AMT/H_2O) had four out of ten objects exhibiting new corrosion signs. From the other treatments, most of the groups exhibited very few tiny spots of active corrosion visible only under the steromicroscope (all of them were classified at level I). Group V (0.01M PMT/EtOH) had tiny spots of corrosion on all of the objects. Similar results were found during the 2004 survey. Tiny corrosion spots visible under the steromicroscope. It is worth mentioning that the renewed corrosion was found on the pits where corrosion commenced during the exposure to high RH the previous year. There is a small question mark as to whether there was actually new corrosion or just corrosion that was not cleaned properly. Also, corrosion pustules might not always be active at the moment of the inspection. In a future year a more detailed survey will be carried out to assess the treatments.

7.2.2 Application of BTA + AMT treatments on Mochlos objects

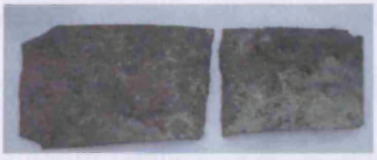
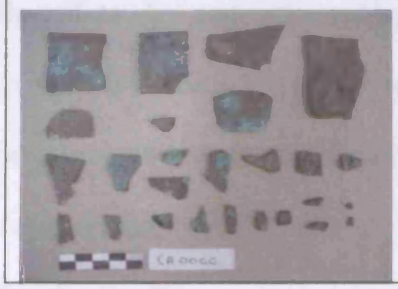
Following the testing in Kaman Kalehoyuk a small number of treatments were tested on objects from the archaeological excavation of Mochlos. The treatments tested were: 0.25M BTA, 0.01M AMT, 0.1M BTA + 0.01M AMT, 0.25M BTA + 0.01M AMT all dissolved in

ethanol. The selection of the treatments was based on the efficiency they displayed in the accelerated corrosion and field tests.

Unlike the objects of Kaman Kalehöyük excavation, these objects were of large dimensions and of significant archaeological importance. The objective was not necessarily to compare the treatments to each other, but foremost to see how the treated objects might behave in the long term. The objects will be eventually displayed in the archaeological museum of Agios Nicolaos.

The archaeological site of Mochlos is situated in eastern Crete. The excavation is located on the coast of Mochlos island and is one of the most important Minoan sites in Crete. The artefacts selected for the testing dated from the Late Minoan period. The bronze artefacts included two bronze bowls (CA 108, and CA109), excavated during 1993, a knife (CA 0066) excavated in 1991 and a saw (CA 0051) excavated in 1992. The type and degree of corrosion suffered by each object was different, reflecting variations in key factors such as their composition, burial conditions, post excavation storage conditions, and previous interventions (see table 7.3).

Table 7.3. The four objects treated with the BTA + AMT treatments from the archaeological excavation of Mochlos, Crete.

Object	Condition	Treatment
Bowls CA 108 and CA 109 	Both bowls were heavily corroded, although of the two, the inner bowl CA 108 appeared to be in better condition. Except of structural damages, both bowls displayed the following: • corrosion blisters • thick crusts of corrosion products • compacted soil crusts • Active corrosion, located beneath outer corrosion layers and within cracks.	CA 108 – 0.25M BTA + 0.01M AMT/EtOH CA 109- 0.1M BTA + 0.01M AMT/EtOH
Saw CA 0051 	In two fragments, both of which display signs of renewed corrosion (bronze disease). There are thick crusts of corrosion products, as well as cracks along the bending zone. Underneath the corrosion crusts, there is the original surface of the object, where use marks have been preserved.	
Knife CA 0066 	Broken into many pieces, Looked totally mineralised. There are numerous corrosion blisters that distort its original shape. Despite previous conservation treatment, there is renewed corrosion as evidenced by the presence of spots of bronze disease throughout the object.	

The testing took place is several stages. Initially the selected objects were mechanically cleaned and in the case of the two bronze bowls they were separated and documented. The objects were not stabilised, in order to assess their state of preservation under controlled storage conditions. Corrosion products were analysed with XRD and identified as copper carbonates (malachite and azurite), copper chlorides (nantokite, atacamite, paratacamite)

and copper oxide (cuprite). The analysis was carried out at the Chemistry Department of University College London.

Before the application of the inhibitors a year later, the objects were examined and it was observed that in spite of the environmentally controlled storage, all four objects presented signs of bronze disease. After the documentation and recording of any changes observed, the objects were treated with mixtures of corrosion inhibitors. The inhibitors used were: BTA, AMT and two combinations of BTA + AMT. Any changes caused by the treatments (such as colour changes) were also documented.

Generally, the treatments did not induce significant colour changes. BTA caused a slight darkening of the surface. The treatments using the BTA + AMT combinations resulted in a formation of yellow precipitate in areas where nantokite was exposed. This yellow powder was easily removed with ethanol. After the application of the solutions, the objects were allowed to dry and were subjected to high relative humidity for 24 hours to examine whether the treatments were successful. None of these presented any signs of active corrosion. After the completion of the inhibition treatments the objects were stored as in the previous year.

The objects were monitored in an annual basis. There were no signs of active corrosion for the next two years. However, during the winter of 2002 the de-humidifier of the storage the objects were placed in broke down and all of the objects were subjected to high levels relative humidity for an unknown period of time (estimated to have been between 2 and 6 months), which resulted in the appearance of bronze disease in all four objects.

This unfortunate event provided a good opportunity to evaluate the efficiency of these inhibitors under high relative humidity conditions. Therefore, the evaluation of the treatments was extremely useful for the objects and the research on inhibitors. The examination revealed that the bowl treated with 0.1M BTA + 0.01M AMT in ethanol had only a few spots of active corrosion, whilst CA-109 treated with 0.25M + 0.1M in ethanol had a lot more new corrosion. The objects treated with 0.01M AMT and 0.25M BTA in ethanol also had new corrosion. The saw especially, which had been treated with the latter, presented extensive corrosion. As has been mentioned earlier, these treatments were not compared for reasons related to the diversity of corrosion forms and corrosion products exhibited.

Another aspect of equal importance that was tackled here was the retreatability of the objects using the same inhibitor mixtures. All four objects were retreated by one hour immersion with 0.1M BTA ++ 0.01M AMT in ethanol. There were no problems regarding the application of the new inhibitor solution. There was formation of yellow precipitate around the active corrosion pits. The objects were stored in the lab for a further 2 years without exhibiting any signs of new corrosion. These objects were coated with a protective coating as they were placed in the museum of Agios Nicholas where they are displayed in totally uncontrolled environmental conditions of high chloride content and fluctuating humidity and temperature levels. The objects will be monitored in the future to record any corrosion or colour changes over the next years.

7.3 Discussion/Conclusions

From the testing undertaken on archaeological objects from Kaman Kalehöyük it is suggested that the factors examined, such as solvent, concentration, time of immersion, and combination of inhibitors, affect to an extent the inhibitive efficiency of a treatment confirming the laboratory experimental results. The length of the time of immersion affects for example the efficiency of BTA similarly to the outcome of the experiments in chapter 5.

In the case of BTA, the number of objects found to be suffering from active corrosion, as well as its extent, is directly related to these factors. The results indicate that BTA at 0.25M is more effective when applied to the object for a smaller amount of time (in this case one hour). The re-use of the solution showed a significant decrease in efficiency under these test conditions in the Kaman Kalehöyük objects. Moreover, the objects treated with the re-used solution have greater colour changes and formation of more BTA crystals on the surface. The same effect was observed in the laboratory tests of re-used solutions of BTA.

The addition of a second inhibitor within the BTA solution affects the protection. In the case of PMT the changes are not great, especially in objects undergoing active corrosion. On the contrary, the addition of AMT increases the inhibitive efficiency of BTA. This is more evident in the lower concentration of BTA. The effect AMT has is more obvious when compared with the results of BTA itself as it can be seen in table 7.2. 0.01M of AMT added into 0.1M BTA in deionised H_2O results in good protection proving the synergistic effect between BTA and AMT is more significant and independent from factors such as

solvent or length of time of immersion that are usually of major significance for BTA treatments.

The results and the assessment are appropriate to the conditions the tests were carried out under at Kaman Kalehöyük. The testing on archaeological objects is a "clinical trial" of the treatments and the final conclusions can only be drawn after long-term monitoring of the treated objects. This is particularly important for the case of BTA + AMT since their combination for use in archaeological conservation appears very promising not only in laboratory experiments but also in these field trials. The objects have to be monitored in regular intervals and the treatments should be re-assessed continuously.

It is therefore suggested every use of the combination for the meantime to be on a trial and experimental basis until these results are verified in the long term with real-life testing.

CHAPTER 8

8 Discussion

All methods used to treat archaeological copper and copper alloys, whether preventive or remedial, aim to slow down the corrosion process. The active corrosion of copper is difficult to halt completely. Stabilisation is necessary when dealing with active corrosion when there is no possibility to use preventive measures to retard the corrosion process. Corrosion inhibitors act by forming a stable copper-inhibitor film that can retard corrosion either by forming a barrier between the metal and its environment preventing access of oxygen to the metal or by altering the corrosion potential of the metal to a more positive value.

Within conservation laboratories it is evident that numerous different BTA treatment methods are currently used for archaeological metal artefacts. There is a need for clarification on this matter. Research on corrosion inhibitors and protective coatings requires an understanding of the corrosion mechanisms as well as the chemistry of the inhibitive compounds and the way they interact.

The objectives of this research were twofold: first to examine the way BTA acts as a corrosion inhibitor for corroded copper, including how selected factors affect the formation (and subsequent efficiency) of a stable Cu-BTA polymer on the surface. And secondly, to

investigate the synergistic effect between BTA and other compounds that could result in increased protection for corroded copper.

The kinetics of the Cu-BTA film growth follow different laws depending on the pH of the solution. Based upon research carried out by Brusic *at al* (1991) in high pH, the film growth follows a logarithmic law, in neutral pH a parabolic law and finally at low pH (approx 2) the film is the result of a dissolution-precipitation mechanism. The thickness of the film formed depends on the surface condition and the laws followed vary accordingly. The formation of a Cu-BTA polymeric film is favoured in neutral or alkaline solutions where copper oxides are more stable. Looking at all the previous studies on BTA not only in the field of conservation but also for industrial applications, one soon appreciates the complexity of the process and how little is actually known about the variables affecting such complex mechanisms.

8.1 Accelerated corrosion testing

The accelerated corrosion testing provided valuable data regarding the behaviour of the tested inhibitor solutions in two different RH, 60 and 95%. There were no remarkable results for coupons exposed to 60% RH highlighting the importance of RH in the corrosion of metals. Most of the assessment was based on the results obtained after exposure of the treated coupons to high RH (95±5%) in a climatic chamber. The fluctuations observed in the chamber used, in high RH were about ±5%. The high HR conditions proved to be very aggressive as most of the treatments failed after only twenty four hours of exposure.

Testing the treatments on both clean and artificially corroded copper coupons was essential for understanding the way different inhibitor compounds react on archaeological objects. Most of the published data refers to clean copper surfaces or surfaces covered with thin air-formed cuprous oxide (cuprite). The presence of aggressive ions (e.g. Cl^-), in most cases is found in solution not as a part of the corrosion products of a metal surface. However, aggressive solutions such as those containing HCl will react with copper to give copper chloride without the presence of an inhibitor.

The experiments with BTA showed that the efficiency is primarily affected by the length of immersion. Time of immersion is related to the pH dropping to more acidic values as measured in chapter 5. It is worth saying that the pH measured was of 0.1M BTA, not 0.25M as it was not soluble in water. There are ways one can measure the pH of partially or non aqueous solutions which however were not possible in this research. Still, the effect of the time of immersion on the efficiency of BTA was remarkable, as in case of aqueous 0.1M BTA solutions extended immersion resulted in acceleration of corrosion.

The effectiveness in ethanoic solutions also dropped to lower values, without having such an extreme effect. BTA in lower concentration (i.e. 0.1M in ethanol) exhibited inhibitive efficiency close to that of 0.25M. The solvent played an important role especially in combination with the time of immersion as mentioned above. The assessment of solutions of even lower BTA concentrations showed some contradictory results which might be related to the fact that inhibition was not complete. As has been discussed in chapter 3, corroded metals require higher inhibitor concentrations. The concentrations used on clean

metals are very low (e.g. 10^{-3}M) in comparison with the concentrations used in conservation, however, in this work an optimum concentration range has been established.

Depending on their mode of action, whether they retard the anodic or cathodic reactions of the corrosion process, insufficient concentration of inhibitor can result in partial coverage of the surface which in case of anodic inhibitors could cause accelerated corrosion. BTA has been reported to act as anodic and/or cathodic inhibitor subject to the solution and the copper substrate. Based on the theory of anodic and cathodic inhibitors discussed in chapter 3, the acceleration of corrosion observed in low concentration BTA solutions could be attributed to BTA being an anodic inhibitor. If BTA was acting as a cathodic (also "safe") inhibitor, the corrosion rate could not exceed that of untreated coupons (see chapter 3).

The effect of the factors examined was verified by analysis. FTIR and XPS analysis showed that BTA partial failure is related to the application method which affects the film formed on the surface, its chemical nature, whether it is a Cu(I) or Cu(II) BTA complex, its thickness, and finally its protective character.

The coupling of the experiments with the analysis showed that the most protective treatment was of 0.25M BTA in ethanol. However, using a 0.1M BTA concentration gave efficiency close to that of 0.25M whilst forming a better defined film attached to the surface copper crystals (observed with SEM). In addition, 0.1M BTA causes less colour changes on the object. It is less expensive and because the concentration used is less, is safer

environmentally, which is something that should be considered in regards to BTA treatments alone.

The re-use of the BTA solutions cause in general decrease in the efficiency of the treatment. Part of this could be related to the pH of the solution which drops to more acidic values after repeated uses.

These results can help determine the most effective ways for using BTA for the treatment of corroded copper artefacts. Regardless of the selection of concentration, ethanol was found to be a better solvent for BTA. However, aqueous solutions, if applied properly, should not be excluded especially since they are safer for the conservator. Coupons treated with aqueous BTA solutions (0.1M) by one hour of immersion had 32% efficiency on average and dropped to -22% increasing the corrosion when left in the solution for twenty four hours. Finally, the length of time of immersion had the greater effect with longer immersion resulting in lower efficiency. In the case of 0.25M in ethanol the efficiency dropped from 67 % to 44 % on average for one and twenty four hours of immersion respectively. The same 30% decrease of efficiency was observed on coupons treated with 0.1M in ethanol where the efficiency dropped from 44 to 31% on average (one and twenty four hours of immersion)>

The use of additives such as AMT in the BTA solutions to improve its efficiency was investigated. The six compounds tested on corroded and clean copper coupons showed that

although not all of these treatments were successful, the idea shows potential especially for the combination of BTA + AMT.

Each of the compounds added to the BTA solution acted in a different way to improve the overall efficiency. Although the experimental conditions were slightly different from those in which some of these compounds were originally tested, the results and trends observed did not always follow what was expected or hoped from previous studies. This also demonstrates the significant difference between clean and corroded metals. The evaluation of these combinations was based on the efficiency in relation to that of each of the inhibitors on its own. A synergistic effect implies that the overall efficiency should be higher than the sum of the efficiency of each of the compounds. Looking at the results of chapter 6, one can see that some of these combinations not only did not improve the overall inhibitive efficiency but also actually increased the corrosion rate in relation to the untreated coupons.

AMT was found effective in short term exposures but in the long term was not as effective. This observation is in agreement with studies on AMT by Faltermeier (1995) and Mohamed *et al* (2004). AMT was used as an inhibitor forming a polymeric film with copper, not as a means to remove chlorides as has been reported by other researchers (Ganorkar *et al*, 1998, Uminski and Guidetti, 1995). The combination of BTA + AMT was not recommended in the literature, however it was found to be the most effective and promising combination in this research. Both AMT and BTA were also effective inhibitors when used alone, however their combination resulted in increased inhibitive efficiency. The

inhibitive efficiency of 0.1M BTA in ethanol for both one and twenty four hour of immersion was increased with the addition of 0.01M AMT by 300%. A similar increase was observed in more concentrated BTA solutions. The addition of AMT in 0.25M BTA solutions resulted in an increase in efficiency of about 100% (see table of BTA + AMT 2 in chapter 6). This increase is even considerable in lower BTA concentrations such as 0.01M BTA in ethanol or deionised water which when used alone are not effective or can even cause an increase in the corrosion rate but with the addition of AMT exhibit inhibitive efficiency of 50% (more than 600% increase).

There was a clear synergistic effect between BTA and AMT as the combination worked even in lower concentrations or when water was used as a solvent. Further to this analysis showed that the improved efficiency is due to the formation of a mainly copper I-inhibitor film which is more stable than one formed with Cu(II). Cu(I)-AMT was mainly formed on coupons treated with AMT with the exception of clean copper where there was some Cu(II)-AMT also present. The treatment of coupons with BTA showed that there is the formation of both Cu(I) and Cu(II) BTA complexes on the surface with the latter being the predominant. BTA on clean copper was found to be bonded to both Cu(I) and Cu(II) in a ratio 2.3 in a 0.1M solution and 0.5 in a 0.25M solution. On corroded copper BTA was mainly bonded to Cu(II), however the Cu^{+}/Cu^{++} ratio varied subject to the concentration of the solution, solvent and the time of immersion. The BTA + AMT treatments resulted in formation of complexes mainly with copper I. The chloride content of the copper-inhibitor film formed on coupons treated with BTA + AMT solutions was found to be lower than

those of BTA or AMT alone. The film formed could be the result of two independent polymers or a copolymer between the two inhibitors and copper.

The addition of amines into the BTA solutions adjusted the pH to neutral or slightly alkaline levels. Their synergism with BTA was largely attributed to the effect they have on the kinetics of the film. In both cases, the film was formed quickly.

BZA is supposed to act not only on the kinetics of the film formation but also on its chemical nature. Since BZA is reported to have more affinity for cupric ions, a cupric complex is formed on the surface (Fleischmann, 1983: 1325). The FTIR and XPS analysis confirmed the presence of Cu(II)-BTA complex, however, all of the BTA + BZA solutions increased the corrosion rate by 15% on average. The treatments also caused great colour alterations on the surface.

Treatment with ETH caused partial dissolution of the corrosion layer and therefore, when measured through weight changes, theoretically exhibited high efficiency. However, this kind of weight change is not considered a positive result. The reported effect of ETH in BTA solutions relates to a fast film formation that could hinder both anodic and cathodic reactions. The results of the first experiment showed that a synergistic effect between the two compounds could be possible, however, the range of the results was such that they are not considered confident for drawing conclusions. Higher concentration BTA + ETH solutions resulted in acceleration of corrosion of corroded copper. The analysis of the BTA + ETH films on different copper substrates showed the presence of a cupric complex. The

presence of ETH in BTA, although able to adjust the pH that could in theory allow BTA to perform better, had the opposite effect on the efficiency. These results and the etching caused to the surface made BZA and ETH unsuitable for further testing on archaeological artefacts.

The experimental results of the BTA + KEX solutions present variations which depended mainly on the concentrations of each compound used. For example, BTA + KEX 1 showed efficiency of the mixture that was higher than that of BTA when used in the same concentration (0.001M) but lower than the efficiency of KEX alone solutions. A synergistic effect between two compounds implies that the outcome will be higher than the sum of that of the compounds when used alone. The fact that BTA efficiency was lower but the efficiency of KEX was higher means there is no synergistic effect, or at least there is no significant synergism between the two compounds. The results at higher concentrations showed that the mixture of BTA + KEX not only did not show any synergism between the compounds but also actually accelerated corrosion. The results of the analysis showed that both inhibitors were present on the surface. KEX formed a Cu(I)-KEX complex on both clean and corroded coupons. The coupons treated with BTA + KEX solutions also presented Cu(I)-KEX and Cu(I)-BTA predominantly. The films formed on both clean and corroded copper were thick, three dimensional and heterogeneous. The reported synergistic effect between BTA and KEX is based on the film formation, either in the formation of two polymeric films complementary to each other, or due to the formation of a xCuBTA·(1-x)CuEtX copolymer (Souto *et al*, 1996: 161-165, Gonzalez *et al*, 1993: 456, Hepel and Cateforis, 2001: 3814). The efficiency of the BTA + KEX treatments has been related to

the degree of surface coverage they provide (Scendo, 2005: 2786). In all reported cases the film was considered to be more compact and protective. The new results show that the efficiency is more related to the adherence of the film into the copper substrate. It is not only the chemical composition of the polymer but how these two compounds interact with each other and the metal to form a complex which produces physical properties that could make it compact and protective. It should also be noted that the surface alterations these treatments caused were ultimately an important reason not to continue experiments using this combination.

The use of halides and more specifically of KI in the corrosion inhibition process has been generally investigated in industry with a variety of inhibitors for different metals. For example, as well as KI added to BTA for copper and/or steel, KI has been proven to act synergistically with 2-mercapto-benzimidazole (MBI) on copper, 1-{(1', 2'-Dicarboxy)ethyl-Benzotriazole on copper (Schweinsberg et al. 1997: 161) and imidazoline derivatives on stainless steel (Ai et al. 2006: 147) . KI has exhibited synergistic effect based mainly on the surface modification it causes to a metal surface and not on the interaction with the organic molecules.

The addition of KI on copper surfaces was supposed to facilitate the adsorption of organic molecules, thereby assisting in a stronger bond between the inhibitor and copper. Although the synergistic effect between BTA and KI is accepted, there are different, often contradictory theories regarding the exact mechanism by which the iodide is adsorbed to the metal surface. The results of the accelerated corrosion tests and the surface analysis

showed that there is indeed a CuI (copper iodide) complex formed on the surface which in combination with the high iodide content found (XPS) indicate the presence of a Cu-I-BTA complex. The ratios between iodide and BTA (N) vary depending on the substrate used. On clean coupons the iodide to BTA ratio was found 0.75 and on corroded copper 1.4. The former is close to that found by Wu (1993: 217) who found the ratio 0.5 and he recommended that the efficiency might be better when this ratio is found in the solution. However, the efficiency of BTA + KI was examined in a variety of concentrations and from those only 0.1M BTA + 0.01M KI in deionised water was found to be effective and to increase the inhibitive efficiency. The concentration and the solvent used affected to a great extent the efficiency. Interestingly, deionised water appears to be better than ethanol. Higher BTA and KI concentrations (like 0.1M BTA + 0.1M KI or 0.25M BTA + 0.1M KI) did not exhibit any synergistic effect, quite the opposite, as the treatments caused acceleration of the corrosion. It is worth mentioning that the BTA + KI combination was the only combination with such varied and contradictory results. The other combinations presented homogeneous results. Some of them worked very well, some worked to an extent and some caused acceleration of corrosion. The BTA + KI combination is the only that although in theory should be working, in practice only one solution worked therefore the BTA + KI efficiency is largely dependent on the concentration and the solvent used. The concentration of the solution needs further investigation. The results indicate that the surface coverage was not sufficient in order to be effective and the partial coverage of the surface could be the explanation to the increase caused to the corrosion rate. The issue of partial coverage was raised by Wu (1993: 209, 216-217) along with the suggestion that the degree of coverage is subject to the concentration and immersion period. The thickness of

BTA + KI was appeared thicker than BTA under SEM (in agreement with Wu, 1993). Electrochemical measurements could shed light to the way this happens on corroded surfaces. Although there was a change in weight even on clean coupons treated with KI, so there is definitely interaction between copper and iodide.

Treatments of 0.005M PMT provided moderate inhibitive efficiency by forming a polymeric Cu(I)-PMT film on the surface. The BTA + PMT treatments were found slightly higher in efficeincy than that of BTA or PMT alone when used in low concentrations (0.005M) exhibiting some synergism between the compounds. In higher concentrations BTA alone was in general more effective, however, there were certain solutions (e.g. 0.1M BTA + 0.1M PMT/EtOH immersed for one hour) that showed that combinations could be effective. The analysis showed the presence of both Cu(I)-BTA and Cu(I)-PMT on the surface. The combination did not cause any significant colour changes and given that it did show moderate efficiency without increasing corrosion, it could be considered "safe" to be applied on archaeological objects for further testing.

Suitability of tested solutions for use on archaeological objects

There are many factors to be considered before applying new treatments on archaeological copper and copper alloy artefacts. It has been already discussed that the results of the laboratory accelerated corrosion testing present certain limitations which relate to the composition of the coupons being 99.9% copper and the formation only of nantokite and cuprite on the corroded coupons. These products do however represent a specific problem

in conservation which is the stabilisation of corrosion when readily reactive nantokite is present.

The results show that certain combinations do not inhibit corrosion, on the contrary they result in an acceleration of the corrosion rate. Chapter 3 discusses the theory behind corrosion inhibitors and uses existing classification systems to explain their mode of action. One classification divides inhibitors into safe and dangerous, depending on whether their use in insufficient concentrations results in more corrosion than if no treatment was applied at all. It is obvious that in the case of archaeological objects, inhibitors that could cause acceleration of the corrosion rate are not acceptable. The aim is always to retard corrosion, if this does not happen either because of insufficient concentration used, or because of incorrect application the compound should not result in a corrosion rate greater than that if the object were left untreated. Thus certain combinations are considered unsuitable for use on real objects. Another important factor with real objects is the colour change observed on the coupons, visible colour changes are largely unacceptable for archaeologically or historically valuable items. For all these reasons only the inhibitors that were found to be safe at the laboratory experiments applied on archaeological objects for further testing and long term monitoring.

It has been shown from the results that the inhibition compounds or mixtures that resulted in the formation of copper I complexes (BTA + AMT, BTA + PMT) were more effective than those that caused formation of copper II complexes (BTA + BZA, BTA + ETH) with

some exceptions. For example, the analysis revealed that other combinations also resulted in the formation of copper (I) inhibitor complex, one example being BTA + KI.

There has been discussion regarding copper I and copper II cations reacting with inhibitors and the degree of protection that each of these provide. It is clear that in case of BTA with AMT there is formation of a film that incorporates both compounds with copper I being the predominant cation or in some cases the only one.

The detection of the copper valence of the copper-inhibitor film is one step towards understanding the mechanisms of film formation and the mode of action of the aforementioned compounds. The properties of the film are affected largely by that but are not governed by it. Other film characteristics are also important such as the polymerisation of the copper-inhibitor film.

A recognised gap or weakness in conservation research is that the chemical composition and the physicochemical properties of the wide range of copper and copper alloys used in antiquity are not always clear. As a result, any new research has to be based on certain assumptions regarding their reactions with inhibitive compounds. Corrosion products of the same composition might have different properties depending on their crystal structure which in turn depends on the conditions under which they have formed (Scott 2002).

Another important issue for the use of inhibitors in conservation is their toxicity. The ubiquitous use in conservation laboratories of a BTA concentration of 3% w/v, although

effective, has been shown by this research to be not the only viable option. The results showed that less concentrated BTA solutions can be effective when applied in a specific manner. The utilisation of synergistic effects by combining inhibitors showed that there are great possibilities for this approach for use on corroded copper objects that could limit the amount of toxic compounds used. For example, in chapter 6, the treatment of 0.01M BTA with 0.01M AMT in water was found to be more effective than any BTA treatment alone. Even without the improved performance of the inhibitors the difference in concentration presents opportunity to limit the amount of harmful compounds used in conservation. Another health and safety related factor is the possibility of the use of deionised water as a solvent, apart from being a more economic solution, it is also safer than other organic solvents for the user. Ethanol is more volatile and during evaporation parts of the inhibitor are also evaporating making the treatment un-safe for the conservator.

No attempt was made to calculate the thickness of the films on the copper substrates. Both XPS and FTIR could be used to calculate thickness however this is subject to surface roughness. The surfaces of the clean coupons were not polished to this extent and the corroded coupon surface was not smooth. Therefore, any attempt to calculate thickness would have been incorrect. Approximate comparisons are based upon SEM images and apparent thickness.

8.2 Colour changes

As mentioned above, colour alterations of the surface caused by conservation treatments are unwelcome and a reason to exclude certain treatments. The aim of corrosion

stabilisation of an archaeological and/or historical object is to retard corrosion but without altering the composition or appearance of its corrosion products. Previously used stabilisation methods are not used anymore because of this. It is important to stabilise corrosion but also to maintain the colours of the original corrosion products as they could provide information to the observer about the object composition, its technological features and the environment it has been exposed to. All these are very important information about the history of the object and should be respected.

The experiments showed that some of the compounds tested caused colour alterations and even if they were effective still they should not be used in conservation because of this. A great deal of the colour alteration observed was due to the formation of precipitates on the coupons. For the purposes of the experiment (explained more comprehensively in the relevant chapters 5 and 6) any precipitates formed on the surface of the coupons were not rinsed off, as is common practice in conservation, as any rinsing would jeopardise the reliability and consistency of the results. Rinsing using solvents and/or cotton swab adds one more factor to be considered, human dexterity, which is uncontrollable and can result in biased results.

For example, the treatment of both clean and corroded copper coupons with KEX and its combination with BTA caused the formation of a thick film the colour and appearance of which was dependent on the concentration and solvent used.

KI also caused colour alterations in certain concentrations. These alterations were more evident in more concentrated solutions and when the coupons stayed immersed for longer

periods (e.g. twenty four hours). Coupons treated with 0.25M BTA and 0.1M KI for twenty four hours presented the biggest colour alteration.

Coupons treated with BTA and PMT did not alter the colour of cuprite, although the surface turned darker. In this combination the biggest colour alterations were observed in less concentrated solutions (e.g 0.005M PMT, 0.005M BTA and 0.005M BTA with 0.005M PMT) where the surface exhibited partly a yellowish tint due to the formation of a precipitate on the surface (see colour measurements in chapter 6 and appendix 3).

8.3 pH effect on corrosion inhibition

Many studies have been devoted to the CuBTA complex formed in different pH environments (Brusic *et al*, 1991, Chen *et al*, 1998, etc.). The kinetics of the film formation are dependent to both the pH of the solution and the surface condition, subsequently the effectiveness of the film is pH-dependent. Irrespective of the type of Cu-BTA complex formed on the surface, BTA provides protection to copper. The pH significance and the reason for its relevance in this research was twofold; firstly, to define the optimum conditions of the Cu-BTA formation in order to maximise the effectiveness of a treatment; secondly to investigate whether adjusting the pH of the BTA solution would promote reactions relating to the film formation and its polymerisation that could provide better protection for an object. It should be noted that the pH of the solution was measured which is a clear indication, however, the pH on the surface and especially the pH in the corrosion pits could differ from that of the solution. For example, pH in corrosion pits can be lower than 2, however this is not easily measured.

From the pH measurements it was clear that the pH of an aqueous BTA solution drops after immersion of copper. The pH of 0.1M BTA dropped from 5.8 to 4.2 after one hour of immersion and to 3.6 after twenty four-hour immersion. This difference might have been directly related to the effectiveness of the treatments as it is reflected in the values of inhibitive efficiency calculated to be 32% and -22% respectively and in the latter case resulting in acceleration of corrosion.

Another aspect of the surface colour of treated objects is public perception of archaeological objects. People generally expect to see green coloured archaeological copper objects, ancient bronzes are no longer highly polished as in antiquity with "restorers" maintaining this polish on an routine basis. The idea of green copper alloys is persistent even with many new sculptures which are patinated in a range of suitable shades to imitate corrosion products. Obviously there is more than aesthetics involved in the patination of bronzes. The formation of a homogenous, both in terms of composition and colour, corrosion layer will also be protective for the underlying metal. The red colour of cuprite, which many of the copper coupons were covered with, is not considered in the same way when found on objects and its discolouration to green or black because of a conservation treatment is not always considered a negative. However, this colour alteration even if pleasant aesthetically is not ethical to modern conservation standards and should be avoided. To day many more relatively unstable copper/copper alloy artefacts receive a heavier protective coating which also darkens the surface.

An important note is that the testing here was on a controlled corrosion surface of cuprite and nantokite and it is possible that other corrosion products might not be discoloured as much by these inhibitors. It should be noted that when dealing with archaeological objects often surfaces are covered with more than one corrosion product, each of which has different composition and colour. However the approach towards inhibitors should ultimately focus on treatments that cause minimum, if any, colour alterations to copper corrosion products. The testing on archaeological objects did not cause great colour alterations, except for darkening caused by more concentrated BTA solutions, and in case of BTA + AMT treatments, formation of a yellow precipitate where nantokite was exposed. The yellow precipitate was not observed on the coupons treated with the solutions in the laboratory. This difference in colour alteration between cuprite-covered copper coupons and corroded objects was also noted in PMT and BTA + PMT treatments.

Testing BTA, AMT, BTA + AMT, PMT and BTA + PMT on the archaeological copper alloy objects was judged acceptable as these compounds did not suggest any risks for the objects (e.g. of accelerating the corrosion rate such as the combination of BTA with KI in certain cases) and also because they did not cause large colour alterations when applied on the corroded coupons.

8.4 Archaeological testing

The testing on archaeological objects from two different sites confirmed the laboratory experiments. The testing in Kaman Kalehöyük was especially valuable as corroboration because of the large number of objects and the fact that these real objects were covered

with many different corrosion products. The object based testing of the selected inhibitors allowed a further comparison between the different treatments as well as evaluation of the factors affecting their effectiveness in real field conditions. More importantly, the field tests were found to be in agreement with the laboratory tests, providing a verification of the results. Factors such as time of immersion, solvent and concentration affected the efficiency of the treatments applied. The most effective treatments were the 0.1M BTA + 0.01M AMT solutions in ethanol and deionised water.

In theory, inhibitors should have access to the metal core in order to be most effective. The results of both the laboratory and field tests in combination with the FTIR and XPS analysis showed that the inhibitors react with metal ions of the corrosion products to form complexes that act protectively. The reactions between the metal ions and the inhibitors is affected by a variety of factors and the surface condition and corrosion products present is one of the most significant. However, there are also exceptions to this, depending on the compound used. Whilst BTA film formation is greatly dependent on the surface condition other inhibitors will form a complex preferably with copper I or copper II in spite of the surface condition.

Following a publication by Golfomitsou and Merkel (2004) on the preliminary investigations of the synergistic effect between BTA and AMT, a few conservators have started to test the combination. They have been advised to use it on a trial basis recording the results and any other comments regarding the treatment.

CHAPTER 9

9 Conclusion

The focus of this thesis has been the assessment of corrosion inhibitors for archaeological copper and copper alloys artefacts. The compounds tested were BTA and solutions of BTA with additives, that might improve the efficiency of BTA through previously reported synergistic effects. The evaluation of the inhibitors was carried out through accelerated corrosion testing in controlled laboratory conditions followed by SEM, FTIR and XPS analysis to understand the inhibition mechanisms. Selected treatments were also assessed on archaeological objects from two sites in Turkey and Greece in real field conditions. The conclusions presented are based on both laboratory accelerated corrosion tests and field tests.

9.1 Benzotriazole

The results showed that variations in application greatly affect the way BTA complexes with copper and subsequently its effectiveness. The copper substrate also plays a significant role. BTA mainly bonds to copper I on clean copper surfaces and primarily to copper II when applied on corroded surfaces. The application factors examined were concentration, time of immersion and the solvent used. The time of immersion was shown to have the

greatest effect in the process, with prolonged immersion causing significant decrease in BTA effectiveness. Also, longer periods of immersion resulted in thicker film formation on the copper surfaces. The composition of the film was found to be mainly Cu(II)-BTA. The Cu^{+}/Cu^{++} ratio as well as the atomic concentration of other species, such as oxygen or chlorides, varied subject to concentration, time of immersion and solvent.

The most effective BTA treatment was found to be a fresh solution of 0.25M BTA in ethanol. The re-use of the BTA solutions showed that the efficiency drops with repeated used of the same solution. The films formed become thicker, heterogeneous and covered partly with porous precipitates. The field tests confirmed these results.

9.2 Synergistic effect

The synergistic effect is extensively exploited for industrial applications, but many successful corrosion inhibitor combinations are not published as they are industrial secrets. Furthermore, specific mechanisms are not always known clearly in detail. There are many factors affecting the synergism between compounds that are not easy to understand. One of the most important issues in synergism for inhibitors is the reactions taking place between the different compounds and the way they interact with the metal surface. Some of these compounds react together and then with the metal, others react independently with the metal resulting in an enhanced film on the metal surface (such as that of BTA and KEX) where the formation of a second polymer could cover "holes" or imperfections of the first film. There are others that react only with the metal with the sole purpose of modifying the

surface in such a way that the other compound can form a more compact and effective complex with it (such as the case of BTA with KI).

From the inhibitors tested a synergistic effect was observed between BTA and AMT. The combination of BTA with AMT was observed to be effective in all solutions tested. AMT although considered an alternative inhibitor for archaeological copper, has not been proven to be effective in long term tests. The synergistic effect between the BTA and AMT was confirmed by the fact that their combinations were found to be more effective in the long run than BTA or AMT in both laboratory and field trials. The BTA + AMT combination worked well even in lower concentrations and in both solvents tested (deionised water and ethanol). The fact that BTA + AMT seem to form a stable complex with copper which is not as dependent on different factors is very promising for use in archaeological conservation.

Apart from the increased efficiency, the use of smaller amounts of toxic or carcinogenic compounds (such as BTA) is very important. Water is also less harmful for the user than solvents such as ethanol or IMS commonly used in conservation. Finally, lower concentrations of compounds in deionised water also substantially reduce the cost of the overall treatment.

The other combinations tested, BTA + BZA, BTA + ETH and BTA + KEX did not present any synergism; on the contrary they caused acceleration of corrosion of the tested coupons. Some of the combinations have to be rejected not only because of the negative result in the

efficiency of the treatment, but also because of colour alterations caused in the corrosion products.

The BTA + KI combination is of particular interest, based on the outcome of the accelerated corrosion testing. BTA + KI treatments resulted in the formation of a thick heterogeneous Cu-I-BTA complex with varied results. One solution showed a synergistic effect between the two compounds, but in general, Cu-I-BTA increased the corrosion rate.

PMT as an inhibitor and its combination with BTA showed some synergism with BTA and it did not accelerated the corrosion rate. In the field tests these treatments were not that effective. Further testing would be required for this combination before its use could be recommended.

9.3 Factors affecting inhibition process

9.3.1 Surface condition

The condition of the copper surface is of major importance for the inhibition process. Variables such as surface condition, corrosion potential, composition of copper alloy, extent of corrosion, corrosion types, composition of corrosion products, presence of aggressive ions such as chlorides and others could affect the interaction and the synergistic effect observed between different compounds. The analytical results verified the significance of these factors.

9.3.2 Concentration

The results of both the accelerated corrosion testing and field tests confirmed in part that higher concentration is more effective for corroded copper. However, although this was the case for BTA, the results from the combination of inhibitors showed that higher concentrations do no always result in more effective treatments. Most of the combinations tested showed decrease of the efficiency at higher concentration solutions.

9.3.3 Time of Immersion

Theoretically the thickness and as often reported, the polymerisation of the film increase with immersion. The results showed that the prolonged period of immersion had the opposite effect in the overall process, especially for BTA treatments. Also, the time of immersion interacted to a great extent with other factors, for example, the solvent used. However, in case of BTA + AMT solutions the effect of the time of immersion was not significant. In some cases longer immersion had a positive effect.

9.3.4 Solvent

Deionised water is rarely used in conservation as a solvent for BTA as its use can reactivate corrosion with devastating consequences. In general ethanol was found to be a better solvent than deionised water and it allows inhibitor films to be produced that are less dependent on other factors, such as the time of immersion. However, the experimental results showed that aqueous solutions can be effective if used properly. In case of BTA, aqueous solutions were found to be relatively effective when used for short times of immersion. In case of BTA + AMT solutions, the treatments were almost equally effective using both solvents.

9.4 Colour alterations

Another important issue is how all these interrelated factors affect not only the film formation and the effectiveness of the treatment but also surface colour alteration which in the case of archaeological objects is of particular importance.

It is imperative when treating archaeological objects that the appearance of the original corrosion products is altered as little as possible. The results show that the degree and extent of surface colour alteration depends largely on the concentration of the solutions and the period of time of immersion. In some cases the immersion period is more important than the actual concentration (as is in the case of BTA with KI, see chapter 6). Therefore, the length of time of immersion plays a significant role in more than one aspects of the inhibition process. It has to be noted that in conservation practice if necessary the surface of a treated object is rinsed with solvent to remove any precipitation or crystals formed on the surface after drying. In this case the surface of the coupons were not rinsed with solvent, they were left to dry. Possibly rinsing of the coupons with solvent after the treatment would have resulted in less significant colour alterations and/or precipitation on the surface. The reason for avoiding such rinsing processes was to avoid variations in the treatments that could cause bias in the results.

All of the tested treatments caused some colour alterations. Alterations caused by BTA treatments were dependent on the solution and the time of immersion. The least colour

changes were observed from the aqueous solutions. In general, shorter immersion times lead to less colour alterations.

The same condition can be applied to all the combinations of BTA with the other compounds. BTA + AMT presented the least colour changes with an occasional slight yellowing of the cuprite layer, followed by BTA + PMT treatments which darken cuprite slightly.

BTA + BZA, BTA + ETH, BTA + KI, BTA+ KEX caused significant colour changes with the last two being drastic. The yellow precipitate observed in the BTA + AMT treatments is attributed to the reaction between AMT and copper chloride as it is not observed on any other areas with different corrosion products.

The testing of selected inhibitors on archaeological objects showed that colour changes are also subject to the composition of the corrosion products. More specifically, BTA treatments applied in high concentrations (0.25M) caused some darkening of the surface. AMT and BTA + AMT treatments resulted in the formation of a yellow precipitate on top of nantokite which was easily removed by solvent. This yellow precipitate was not observed on the testing coupons. PMT and BTA + PMT treatments, although did not present significant colour changes of the testing coupons in the laboratory experiments, they caused the formation of a whitish precipitate on the surface of the objects which was simply removed by solvent rinsing of the surface.

As it has been mentioned in the relevant chapter, the negative results in certain cases should not discourage further testing of some of these compounds to define the best parameters under which they could be effective.

New commercial products promising to halt corrosion are often presented to the market, but with no thorough understanding of their mode of action (which may be considered an industrial secret). These products should not be used in the conservation of cultural heritage artefacts. The results of this research showed that there are many factors to be considered as well as interactions between different factors which may not have been taken into account with commercial products designed for different purposes.

9.5 Further research

This thesis may also serve as the introduction to further and more advanced research on specific parameters relating the synergistic effect between corrosion inhibitors for use in the conservation field. The physicochemical parameters are yet to be established in detail.

This research examined some compounds that presented a synergistic effect when used together. The synergistic effect is used extensively in commercial corrosion inhibitors, the compositions of which are not widely known. However, there are certain results that could be utilised for further research in the field of inhibitors for archaeological copper and copper alloys. Often commercial products can contain more than even two inhibitors, for example some automotive radiator coolant solutions pass through multiple metal

compartments and so contain multiple inhibitors. There is much more scope for "designing" inhibitor solutions for archaeological metals.

BTA is obvious a very effective inhibitor and it is not accidental that it is still in use so many years after it was first proposed for conservation. Its infrequent failure to protect copper is due to a number of reasons, some of which can be easily surpassed either by modifying the application methodology (e.g. the time of immersion) or by adding compounds that could act synergistically with BTA and would help in the process.

The compounds tested had a different effect in their overall mechanisms of action. Some adjusted the pH to neutral or slightly alkaline values, others affected the film formed, the degree of polymerization, etc. There are a lot more compounds that could influence positively the inhibition process. The next step in terms of BTA would be to test more additives to find those that give a synergistic effect.

An important next step to this research is to understand more about the reaction between these compounds. Analytical techniques such as NMR could examine how these inhibitors interact and if they form a co-polymer or different polymers. This answer could lead to a new series of experiments with modelling of the molecular structures for better multiple inhibitors.

The pH was found to be of vital importance for the inhibitor film formation on copper. Therefore, more detailed pH measurements using a probe connected to a computer program

that would allow recording of the value at short intervals (e.g. per minute) could allow a better understanding and evaluation of the optimum range of time of immersion.

Electrochemical testing is also considered necessary. Cyclic voltammetry measurements of the different compounds were carried out during the course of this thesis, however, the results were not clear and were not included in the thesis. Measurements using linear scan potential voltammetry, impedance spectroscopy and other electrochemical methods could help understand more the mode of action of these inhibitors including whether they are anodic or cathodic inhibitors. For example, potentiometric measurements of the different corrosion inhibitors and mixtures of compounds over a period of 24 hours could show the time needed to form a more stable film and when this stops to be effective. It is a fact that BTA in all solutions tested stopped being as effective after a certain length of immersion time, so investigations to find the threshold for its maximum efficiency are very important.

The behaviour of different corrosion products treated with different compounds is of major importance. The reaction of corrosion inhibitors with corrosion products could be investigated with the treatment of single compounds in powder form with inhibitors, which would then be analysed using FT-IR. This analysis would examine how the film formation is affected by the corrosion product present on the surface of an object and could be then followed by analysis of more complicated corroded surfaces. Comparative studies between the two could further the understanding of corrosion inhibition on such surfaces. A microbalance could be used to measure water absorption of corrosion products before and

after the treatments. This would help to characterise better the behaviour of certain compounds under different conditions.

Research should also focus on more eco-friendly and preferably non-toxic compounds as corrosion inhibitors for copper. The use of the synergistic effect can easily open a whole new range of materials that are not used up to now or are not effective as inhibitors when used alone. There is a large number of compounds that could successfully inhibit corrosion if used in combination with others. For example, Zhang et al (2003: 361) have found a synergistic effect between 2-mercapto-benzimidazole (MBI) and KI, Schweinsberg et al. (1997: 161) found synergistic effect between 1-{(1', 2'-Dicarboxy)ethyl-Benzotriazole and KI in sulphuric acid for copper corrosion inhibition. There is a whole range of materials that could be utilised and research should take advantage of the synergistic effect to proceed in the testing of non-toxic inhibitors. Caffeine has been tested as a corrosion inhibitor for copper (Fallavena et al, 2006). Tobacco leaves are also currently being tested (Argyropoulos, PROMET project 2005). Natural honey has also been tested as an inhibitor for copper. However, one of the most common problems when using natural products is that the composition will vary depending on the preparation of the solution.

One of the most important issues is to understand the mechanisms involved in the inhibition of corroded surfaces. By examining the corrosion of metals in greater depth and understanding the chemistry, structure and properties of the corrosion products, research can focus on more suitable compounds and combinations of compounds.

The efficiency is dependent not only on the chemical composition of the polymeric film formed on the copper surface but also on the film's growth kinetics. The time of immersion was one of the most important factors affecting the film formation. Studies on the kinetics of the film formation using ellipsometry could help identify the parameters that could enable better efficiency.

Temperature is another factor affecting the inhibition process. Its effect in certain non-toxic aqueous solutions could also be examined.

This research examined only a few compounds that could act synergistically. Other compounds when used together might have synergistic effect that could result in new treatments.

One of the key points is that the condition of copper surfaces affects to a great extent the reactions taking place between copper and inhibitors. Therefore, any compounds must be tested on both clean and corroded copper to investigate the exact conditions under which a compound is effective. Also, the testing conditions and the application methodology are of paramount importance and should not be ruled out of any testing methodology.

The toxicity of BTA has been the subject of research in industry. BTA is considered harmful by the suppliers. Its toxicity has been tested on a number of micro organisms (see chapter 3). However, in the conservation field speculations about its toxicity are based on outdated literature, not in recent scientific investigations. Even so, the facts about its

relevant toxicity exist in other fields and more research is necessary, not only for BTA but for other materials including inhibitors, solvents, adhesives and protective coatings used in conservation.

List of References

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Ai, J.Z., Guo, X.P., Qu, J.E., Chen, Z.Y. and Zheng J.S. 2006. Adsorption behavior and synergistic mechanism of a cationic inhibitor and KI on the galvanic electrode, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **281**(1-3), 147-155

Ammelinckx, S., Van Dyck, D. Van Landuyt, J. and Van Tendeloo, G. 1997. *Electron Microscopy: Principles and Fundamentals*. VCH Verlag

Ammeloot, F., Fiaud, C. and Sutter, E.M.M. 1997. Application of Photoelectrochemical methods for the Characterization of Cu(I) oxide layers modified in the presence of Corrosion Inhibitors. *Electrochimica Acta,* **42**(23-24), 3565-3574.

Ammeloot, F., Fiaud, C. and Sutter, E.M.M. 1999. Characterization of the Oxide Layers on a Cu-13Sn Alloy in a NaCl aqueous Solutions without and with 0.1M Benzotriazole. Electrochemical and Photoelectrochemical Contributions. *Electrochimica Acta,* **44**, 2549-2558.

Andreozzi, R., Caprio, V., Insola, A. and Longo, G. 1998. Photochemical Degradation of Benzotriazole in Aqueous Solution, *Journal of Chemical Technology and Biotechnology,* **73**, 93-98

Angelucci, S., Fiorentino P., Kosinkova J. and Marabelli, M. 1978. Pitting Corrosion in

Copper and Copper Alloys: Comparative Treatment Tests, *Studies in Conservation*, **23**, 147-156.

Argyropoulos, V. 2004. *Personal Communication.*

Bacon, L. and Janporsi, K. 1977. The Thai Bronze Project, *Studies in Conservation,* **22**(1), 32-39.

Bastidas, J.M. and Otero, E. 1996. A Comparative Study of Benzotriazole and 2-Amino-5 Mercapto-1,3,4-Thiadiazole as Copper Copper Inhibitors in Acid Media, *Materials and Corrosion*, **47**, 333-337.

Bercudou, M. 1996. Introduction to Archaeological Conservation, in N. S. Price, M. K. Talley and A. Melucco Vaccaro (eds), *Historical and Philosophical Issues in the Conservation of Cultural Heritage*, 248-260. Los Angeles: The Getty Conservation Institute.

Bigotto, A., Pandey, A. N. and Zerbo, C.1996. Polarised Infrared and Raman Spectra and Ab-Initio Calculations of Benzotriazole, *Spectroscopy Letters*, **29**(3), 511.

Box, G.E.P., Hunter, W.G. and Hunter, J.S. 1978. *Statistics for Experimenters: an Introduction to Design, Data Analysis, and Model Building.* Chichester: John Wiley & Sons.

Brazil, R. 1999. *An Investigation into the Use of Corrosion Inhibitive Treatments for the Conservation of Archaeological Iron.* Unpuplished PhD thesis, London: UCL.

Briggs, D. and Riviere, J.C. 1994. Spectral Interpretation in *Practical Surface Analysis*, edited by Briggs, D. and Seah M.P. (eds.) Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy, 2nd Ed. Chichester: John Wiley & Sons, 85-141.

Brostoff, L.B. 1997. Investigation into the Interaction of Benzotriazole with Copper Corrosion Minerals and Surfaces. In MacLeod, I.D., Pennec, S.L. and Robbiola, L. (eds). *Metal 95, Proceedings of the International Conference on Metals Conservation, Semur-en-Auxois, 25 - 28 Sept. 1995.* London : James & James. 99-108

Brusic, V., Frisch, M.A., Eldridge, B.N., Novak, F.P., Kaufman, F.B., Rush, B.M. and Frankel, G.S. 1991. Copper Corrosion with and without Inhibitors, *Journal of the Electrochemical Society*, **138**(8), 2253-2258.

Brusic, V., Angelopoulos, M. and Graham, T. 1997. Use of Polyaniline and Its Derivatives in Corrosion Protection of Copper and Silver, *Journal Of the Electrochemical Society*, **144**, 436-442.

Burns, D.A. and Ciurczac, E.W. 2001. *Handbook of Near-Infra-Red Analysis*, 2nd Ed. New York: Dekker.

Carney, T. 2006. Personal Communication.

Carter, V.E. 1982. *Corrosion Testing for Metal Finishing.* London: Butterworths Heinemann (Published in Association with The Institute of Metal Finishing).

Chadwick, D. and Hashemi, T. 1978. Adsorbed Corrosion Inhibitors Studied by Electron Spectroscopy : Benzotriazole on Copper and Copper Alloys, *Corrosion Science*, **18,** 39-51.

Champion, F.A. 1964. *Corrosion Testing Procedures*, 2nd Edition. London: Chapman and Hall.

Chawla, S.K., Rickett, B.I., Sankarraman, N. and Payer, J.H. 1992. An X-Ray Photoelectron Spectroscopic Investigation of the Air-Formed Film on Copper, *Corrosion Science,* **33**(10), 1617-1631 .

Chen, J-H., Lin, Z-C., Chen, S., Nie, L-H. and Yao S-Z. 1998. An XPS and BAW Sensor Study of the Structure and Real-Time Growth Behaviour of a Complex Surface Film on Copper in Sodium Chloride Solutions (pH=9) Containing a Low Concentration of Benzotriazole, *Electrochimica Acta*, **43**(3-4), 265-274.

Cohen, S.L. Brusic, V.A., Kaufman, F.B., Frankel, G.S., Motakef, S. and Rush, B. 1990. X-ray Photoelectron Spectroscopy and Ellipsometry Studies of the Electrochemically

Controlled Adsorption of Benzotriazoel on Copper Surfaces, *Journal of Vacuum Science and Technology A,* **8**(3), 2417-2424.

Combarieu, R., Dauchot, G. and Delamare, F. 1998. Etude de l' Adsorption du Benzotriazole sur le Fer, le Cuivre et le Laiton a par Tof-SIMS et XPS in Mourey, W and Robbiola, L (eds.) *Metal 98 27-29 May 1998 Draguignon-Feganieres, France*, 223-228. London : James and James.

Colthup, N.B., Daly, L.H. and Wiberley S.E.1990. *Introduction to Infra-red and Raman Spectroscopy* 3rd ed. London : Academic Press.

Cotton, J.B. and Scholes, I.R. 1967. Benzotriazole and Related Compounds as Corrosion Inhibitors for Copper, *British Corrosion Journal*, **2**, 1-5.

Craig, B.D. 1991. *Fundamental Aspects of Corrosion Films in Corrosion Science*. New York: Plenum Press.

Cronyn, J.M. 1996. *The Elements of Archaeological Conservation.* London: Routledge.

Debe, M.K. 1984. Extracting Physical Structure Information from Thin Organic Films With Reflectancd Absortbtion Infrared Spectroscopy, *Journal of Applied Physics,* **55**(9), 3354-3366.

Degrigny, C and Spiteri, L. 2004. Electrochemical Monitoring of Marine Iron Artefacts during their Storage/Stabilisation in Alkaline Solutions. In Aston J. and Hallam D.(eds.) *Metal 04- Proceedings of the International conference on Metals Conservation Canberra, Australia , 4-8 October 2004*, 344-368. Canberra: National Museum of Australia.

Drayman-Weisser, T. 1987. The Use of Sodium Carbonate as a Pretreatment for Difficult-to-Stabilise Bronzes, in J Black (ed.), *Recent Advantages in the Conservation and Analysis of Artefacts*, 105-8. London: Summer School Press.

Dugdale, I. and Cotton, J.B. 1963. An Electrochemical Investigation on the Prevention of Staining of Copper by Benzotriazole, *Corrosion Science*, **3**, 69-74.

Evans, UR. 1960. T*he Corrosion and Oxidation of Metals.* London: Edward Arnold.

Evans, U.R. 1981. *An Introduction to Metallic Corrosion.* 3rd ed. London: Edward Arnold.

Fang, B-S., Olson, C. and Lynch, D.W. 1986. A Photoemission Study on Clean and Copper and Cuprous Oxide, *Surface Science,***3**, 476-490.

Fallavenna, T., Antonow, M. and Simoes Gonalves. 2006. Caffeine as non-toxic inhibitor for copper in aqueous solutions of potassium nitrate, *Applied Surface Science,* In press, Available on line 23 January 2006.

Faltermeier, R.B. 1995. *The Evaluation of Corrosion Inhibitors for Application to Copper and Copper Alloy Archaeological Artefacts.* PhD Thesis, University College London, London.

Fiaud, C. 1995. Inhibition of Copper Corrosion. The Complementary Role of Oxides and Corrosion Inhibitors. *Proceedings of the 8th European Symposium on Corrosion Inhibitors (8SEIC)* , 929-49, Ferrara, Italy.

Fischer, W.R., Wagner, B.D., Siedlarek, H., Fübinger, B., Hänbel, I and von der Bank, N. 1997. In MacLeod, I.D., Pennec, S.L. and Robbiola, L. (eds). *Metal 95, Proceedings of the International Conference on Metals Conservation, Semur-en-Auxois, 25 - 28 Sept. 1995.* London : James & James. 89-94.

Fleischmann, M., Hill, I.R., Mengoli, G. and Musiani, M.M. 1983. The Synergistic Effect of Benzylamine on the Corrosion Inhibition of Copper by Benzotriazole, *Electrochimica Acta* **28**, 1325-1333.

Fleischmann, M., Hill, I.R., Mengoli, G., Musiani, M.M. and Akhavan, J. 1985. A Comparative Study on the Efficiency of some Organic Inhibitors for the Corrosion of Copper in Aqueous Chloride Media Using Electrochemical and Surface Enhanced Raman Scattering Techniques, *Electrochimica Acta*, **7**, 879-88.

Fleischmann, M., Mengoli, G., Musiani, M.M. and Ragura, C. 1985. An Electrochemical

and Raman Spectroscopic Investigation of Synergistic Effects in the Corrosion Inhibition of Copper, *Electrochimica Acta,* **30**, 1591-602.

Fontana, M.G. 1986. *Corrosion Engineering.* 3rd ed. London: McGraw-Hill.

Fox, P G, Lewis G and Beden P J, 1979. Some Chemical Aspects of the Corrosion Inhibition of Copper by Benzotriazole, *Corrosion Science*, **19**, 457-467.

France-Lanord, A, 1996. Knowing How to "Question" the Object Before Restoring it, in N S Price, M K Talley and A Melucco Vaccaro (eds.), *Historical and Philosophical Issues in the Conservation of Cultural Heritage*, 244-47, Los Angeles: The Getty Conservation Institute.

Gajendragad, M. and Agrawala, U. 1975. Complexing Behaviour of 5-Amino-2-thiol-1, 3, 4-thiadazole; Part III. *Indian Journal For Chemistry*, **13**, 1331-1334.

Gajendragad, M. and Agrawala, U. 1975. Complexing Behaviour of 5-Amino-1, 3, 4-Thiadiazole-2-thiol. II Complexes of Ni(II), Rh(I), Pd(II), Pt(II), Au(III) and Cu(II), *Bulletin of the Chemical Society of Japan* **48**, 1024-1029.

Ganorkar, M.C., Panditrao, V., Gayathri, P. and Sceenivasa Rao, T.A. 1988. A Novel Method for Conservation of Copper-Based Artifacts, *Studies in Conservation* **33**, 97-101.

Golfomitsou, S. and Merkel, J.F. 2004. Synergistic Effects of Corrosion Inhibitors for Copper and Copper Alloy Archaeological Artefacts in Aston J. and Hallam D.(eds.) *Metal 04- Proceedings of the International conference on Metals Conservation Canberra, Australia , 4-8 October 2004*, 344-368. Canberra: National Museum of Australia.

Gomez Becerra, J., Salvarezza, R.C. and Arvia, A.J. 1987. Electrochemical Behaviour of Copper in Aqueous Solution Containing Potassium Ethylxanthate, *Journal of Applied Electrochemistry,* **17**, 779-788.

Gonzalez, S., Laz, M. M., Souto, R. M., Salvarezza, R C and Arvia, A J 1993 Synergistic Effects in the Inhibition of Copper Corrosion, *Corrosion*, **49**(6), 450-456 .

Grove, D,M. and Davis T. 1992. *Engineering, Quality, and Experimental Design.* Harlow, Essex: Longman Scientific & Technical.

Hawley, J.K. 1996. Celtic finds in basel: Testing the conservator's Stamina. In *Archaeological Conservation and Its Consequences.* Ed. Roy, A and Smith, P. London: IIC, 76-81.

Heitz, E., Henkhaus, R. and Rahmel, A. 1992. *Corrosion Science, an Experimental Approach.* translators: Dr. Waterhouse, R.B, transl.editor Dr. Holnes, D.R. England: Ellis Horwood Limited

Hepel M. and Cateforis E. 2001. Studies of Copper Corrosion Inhibition Using Electrochemical Quartz Crystal Nanobalance and Quartz Crystal Immitance Techniques, *Electrochimica Acta*, **46** (24), 3801-3815.

Jiang, Y., Adams, J.B. and Sun, D. 2004. Benzotriazole Adsorption on $Cu_2O(111)$ Surfaces: A First Principles Study, *Journal of Physical Chemistry*, **108**, 12851-12857.

Jones, D.A. 1996. *Principles and Prevention of Corrosion.* 2nd ed. Upper Sandle River, New Jersey: Prentice Hall Inc.

Kertit, S., Es-Soufi H., Hammouti, B. et Benkaddour, M. 1998. 1-Phenyl-5-Mercapto-1, 2, 3, 4-Tétrazole (PMT) : Un Nouvel Inhibiteur de Corrosion de l' Alliage Cu-Zn Efficace à Très Fiable Concentration. *Journal De Chimie Physique*, **95**, 2070-2082.

Kuznetsov, Y.I. 1996. *Organic Corrosion Inhibitors of Metals.* New York: Plenum Press.

Leygraf, C. and Graedel, T. 2000. *Atmospheric Corrosion.* Chichester: John Wiley & Sons.

Li, H-H., Chen, Z-R., Li, J-Q., Zhan, H-B., Zhang, W-X., Huang, C-C., Ma, C. and Zhao, B. 2006. Synthesis, Structure and Optical Limiting Effect of a Novel Inorganic-Organic Hybrid Polymer containing Mixed Chains of Copper (I)/Iodine, *Journal of Solid State Chemistry*, **179**(5), 1415-1420.

Lorenz, W.J. and Mansfeld, F. 1986. Interface and Interphase Corrosion Inhibition, *Electrochimica Acta,* **31**, 467-476.

Madsen, H.B. 1967. A Preliminary Note on the Use of Benzotriazole for Stabilizing Bronze Objects, *Studies in Conservation,* **12**(4), 163-66.

Magaino, S., Sobue, K., Kawaguchi, A. and Sasaki, Y. 1998. Effect of Benzotriazole Pretreatment on Corrosion Resistance of Polymer Coated Copper under Acid-Rain Environment, *Denki Kagak,* **66**(2), 217-218.

Mansfeld, F. and Smith, T. 1973. Technical Note: Benzotriazole as Corrosion Inhibitor for Copper. II. Acid NaCl Solutions, *Corrosion,* **29**(3), 105-107.

Mansefeld, F., Smith T. and Parry E.P. 1971. Benzotriazole as Corrosion Inhibitor for Copper, *Corrosion,* **27**, 289-294.

Mendoza, A.R., Corvo, F., Gómez, A. and Gómez. J. 2004. Influence of the corrosion products of copper on its atmospheric corrosion kinetics in tropical climate, *Corrosion Science,* **46**(5), 1189-1200

Metikoš-Huković, M., Babić, R. and Paić, I. 2000. Copper Corrosion at Various pH Values with and without the Inhibitor, *Journal of Applied Electrchemicstry,* **30**, 617-624.

Mihit, M., El Issami, S., Bouklah, M., Bazzi, L., Hammouti, B., Ait Addi, E., Salghi, R., and Kertit, S. 2006. The inhibited effect of some Tetrazolic Compounds Towards the Corrosion of Brass in Nitric Acid Solution, *Applied Surface Science*, **252**(6), 2389-2395

Millet, B., Fiaud, C., Hinnen, C. and. Sutter. E.M.M.1995. A Correlation between Electrochemical Behaviour, Composition and Semiconducting Properties of Naturally Grown Oxide Films on Copper, *Corrosion Science*, **37**(12), 1903-1918.

Mirambet, F. 2004. Personal Communication.

Mohamed, W.A., Raheb, N.M. and Shakour, A.A. 2004. Performance of Copper Corrosion Inhibitors in a Museum Environment – A Comparative Study Using FTIR Spectroscopy, in Aston J. and Hallam D.(eds.) *Metal 04- Proceedings of the International conference on Metals Conservation Canberra, Australia , 4-8 October 2004.* 369-378. Canberra: National Museum of Australia.

Montgomery, D. 1997. *The Design and Analysis of Experiments.* 4th ed. New York: John Wiley and Sons.

Morgan, E. 1991. *Chemometrics: Experimental Design.* New York: John Wiley & Sons.

Musiani, M.M., Mengoli G., Fleischmann M. and Lowry R.B. 1987. An Electrochemical and SERS Investigation of the Influence of pH on the Effectiveness of Some Corrosion

Inhibitors of Copper, *Journal of Electroanalytical Chemistry,* **217**, 182-202.

Nilsson, J.-O., Tornikvist, C. and Liedberg, B. 1989. Photoelectron and Infrared Reflection Absorption Spectroscopy of Benzotriazole Adsorbed on Copper and Cuprous Oxide Surfaces, *Applied Surface Science* **37**, 306-326.

Oddy, W.A. 1972. On the Toxicity of Benzotriazole, *Studies in Conservation,* **17**, 134-35.

Oddy, W.A. 1974. Toxicity of Benzotriazole, *Studies in Conservation,* **19**, 188-189.

Oddy, W.A. and Hughes, M.J. 1970. The Stabilization of "Active" Bronze and Iron Antiquities by the Use of Sodium Sesquicarbonate, *Studies in Conservation,* **15**, 183-89.

Ohno, Y. 2000. CIE Fundamentals for Color Measurements in *Proceedings of the International Conference on Digital Printing Technologies, Oct. 15-20, 2000, Vancouver, Canada,* 540-545.

Organ, R.M. 1963. Aspects of Bronze Patina and its Treatment, *Studies in Conservation,* **8**, 1-9.

Organ, R.M. 1992. Corrosion, Use it or Lose it? in E. A. Sanpaolo (ed) *Archaeometallurgia Ricerdre e Prospettive.Atti del Coloquio Internazionale de Archeometallurgia,* 423-435, n.d.

Organ, R.M. 1977. The Current Status of the Treatment of Corroded Metal Artefacts, in B.F. Brown, H.C. Burnett, W.T. Chase, M. Goodway, J. Kruger, and M. Pourbaix (eds), *Corrosion and Metal Artefacts. A Dialogue Between Conservators and Archaeologists and Corrosion Scientists,. A Dialogue Between Conservators and Archaeologists and Corrosion Scientists*, 107-142. Washington: NACE.

Organ, R.M. 1961. A New Treatment for "Bronze Disease", *The Museum Journal,* **61**, 54-56.

Orton, C. 2000, 2006. Personal Communication.

Otero and Bastidas. 1996. Cleaning of Two Hundred Year Old Copper Works of Art Using Ctiric Acid With and Without Benzotriazole and 2-Amino-5-mercapto-1, 3,4-thiadiazole *Materials and Corrosion* , **47**, 133- 138.

Plenderleith, H.J. and Werner A.E.A. 1971. *The conservation of Antiquities and Works of Art. Treatment, Repair and Restoration.* 2nd ed. London: Oxford University Press.

Poling, G.W. 1970. Reflection Infrared Studies of Films Formed by Benzotriazole on Copper (or Cu), *Corrosion Science*, **10**, 359-70.

Pourbaix, M. 1966. *Atlas of Electrochemical Equilibria in Aqueous Solutions.* London: Pergamon Press.

Putilova, I.N., Balezin, S.A. and Barannik, V.P. 1960. *Metallic Corrosion Inhibitors.* London: Pergamon Press.

Ratner, B. D. and Castner, D.G. (eds) 1997. *Surface Modification of Polymeric Biomaterials: Proceedings of the American Chemical Society Division of Polymer Chemistry International Symposium on Surface Modification of Polymeric Biomaterials, April 2-6, 1995, Anaheim, California.* New York: Plenum Press.

Riggs, O.L.Jr, 1981. Theoretical Aspects of Corrosion Inhibitors and Inhibition, in C C Nathan (ed), *Corrosion Inhibitors*, 7-27, Texas, Houston: National Association of Corrosion Engineers (NACE).

Robbiola, L., Blengino, J.-M. and Fiaud, C. 1998. Morphology and Mechanisms of Formation of Natural Patinas on Archaeological Cu-Sn Alloys , *Corrosion Science*, **40**(12), 2083-2111.

Roberts, R.F. 1974. X-Ray Photoelectron Spectroscopic Characterisation of Copper and Copper Oxide Surfaces Treated with Benzotriazole, *Journal of the Electron Spectroscopy and Related Phenomena*, **4**, 273-91.

Rodgers, B.A. 2004. *The Archaeologist's Manual for Conservation: A Guide to Non-Toxic Minimal Intervention Artifact Stabilisation.* New York: Kluwer Academic/Plenum

Publishers.

Rozenfeld, I.L. 1981. *Corrosion Inhibitors*. USA: McGraw-Hill Inc.

Saaty, T.L. 1990. *The Analytic Hierarchy Process*. Pittsburgh: RWS Publications.

Safety (MSDS) Data for Zinc Selenide, 2006. In http://physchem.ox.ac.uk/MSDS/ZI/ zinc_selenide.html

Sastri, V.S. 1998. *Corrosion Inhibitors, Principles and Applications*. Canada: John Wiley and Sons.

Scheifler, L.G. 1985. Vapour Phase Inhibitors: A Review of their Use for Corroded Copper and Copper Alloys, in S Keene (ed), Corrosion Inhibitors in Conservation, *British Museum Occasional Paper*, **4**,36-43.

Schweitzer, P.A. (ed), 1989. *Corrosion and Corrosion Protection Handbook*. New York: MarcelDekker, Inc.

Scendo, M. 2005. Potassium Ethyl Xanthate as a Corrosion Inhibitor for Coppper in Acidic Chloride Solutions, *Corrosion Science*, **47**(7), 1738-1749.

Schweitzer, P.A. 1998. *Encyclopedia of Corrosion Technology*. New York: Marcel Dekker,

INC.

Schweinsberg, D.P., Bottle, S.E., Otieno-Alego, V. and Notoya, T.A. 1997. Near-Infrared FT-Raman (SERS) and Electrochemical Study on the Synergistic Effect of 1-{(1', 2'-Dicarboxy)ethyl-Benzotriazole and KI on the Dissolution of Copper in Aerated Sulfuric Acid, *Journal of Applied Electrochemistry*, **27**, 161-168.

Scott, D.A. 1990. Bronze Disease:A Review of some Chemical Problems and the Role of Relative Humidity, *Journal of the American Institute for Conservation,* **29**, 193-206.

Scott, D.A. 2002. *Copper and Bronze in Art: Corrosion, Colorants, Conservation.* Los Angeles: Getty Conservation Institute.

Sease, C. 1978. Benzotriazole: A Review for Conservators, *Studies in Conservation*, **23**, 76-85.

Sherman, F. 2004. Personal Communication.

Shreir, L.L., Jarman R.A. and Burstein, G.T. 1994. *Corrosion 2: Corrosion Control.* 3rd ed. Oxford: Butterworths-Heinemann Ltd.

Skerry, B.S. 1985. How Corrosion Inhibitors Work, in S Keene (ed), Corrosion Inhibitors

in Conservation, *British Museum Occasional Paper*, **4,** 5-12.

Smith, B. 1998. *Infrared Spectral Interpretation - A Systematic Approach*, Boca Raton: CRC Press Inc.

Souto, R.M., Fox, V., Laz, M.M., Prez, M, and González, S. 1996. Some experiments regarding the Corrosion Inhibition of Copper by Benzotrizaole and Potassium Ethyl Xanthate, *Journal of Electroanalytical Chemistry,* **411**, 161-165.

Souto, R.M., Laz M.M. and González, S. 1997. X-ray Photoelectron Spectroscopy and Electrochemical Studies on the Interaction of Potassium Ethyl Xanthate with Metallic Copper, *Journal of Physical Chemistry,* **101,** 508-511.

Stuart, B. 1996. *Modern Infrared Spectroscopy*. Chichester: John Wiley and Sons.

Stupnišek-Lisak, E., Kopjar, D. and Mance A. D. 1998. The Inhibition of Copper Corrosion in Acid Media, *Bulletin of Electrochemistry*, **14**, 10-15.

Stupnišek-Lisak, E., Lončaric Božić, A. and Cafuk, I. 1998. Low Toxicity Copper Corrosion Inhibitors, *Corrosion*, **54**(9), 713-20.

Suenson-Taylor, K., Sully, D. and Orton, C. 1999. Data in Conservation: The Missing Link in the Process, *Studies in Conservation,* **44**,184-194.

Taylor, R.J. and MacLeod, I.D. 1985. Corrosion of Bronzes on Shipwrecks. A Comparison of Corrosion Rates Deduced from Shipwreck Material and from Electrochemical Methods, *Corrosion*, **41**, 100-104.

Timar-Balazsy, A. and Eastop, D. 1997. *Chemical Principles of Textile Conservation.* Oxford, Boston: Butterworth-Heinemann.

Turgoose, S. and Duncan, S.J. 1992. Techniques for Metal Sculpture Corrosion Inhibition, in T Drayman-Weisser (ed), *Dialogue/89- The Conservation of Bronze Sculpture in the Outdoor Environment: A Dialogue Among Conservators, Curators, Environmental Scientists, and Corrosion Engineers*, 275-278, Texas, Houston: NACE.

Twilley, J. 1996. Scientific Analysis of Six Bronze Fibulae from Kaman Kalehöyük. *Anatolian Archaeological Studies V*, 237-250.

Uhlig, H.H. and Revie, R.W. 1985. *Corrosion and Corrosion Control. An Introduction to Corrosion Science and Engineering.* New York: John Wiley and Sons.

Uminski, M. and Guidetti, V. 1995. The Removal of Chloride Ions from Artificially Corroded Bronze Plates. *Studies in Conservation*, **40**. 274-278.

Xu, Z., Lau, S. and Bohn, P.W. 1993. The Role of Nitrogen and Silfur Heterocycles in

Corrosion Inhibition. 1. Initial Steps in the adsorption of Benzotriazole at Copper(I) and Copper(II) Oxides. *Langmuir,* **9**, 993-1000.

Wagner, D.H.J., Kropp, M., Fisher, W.R. and Kars, H. 1998. A Systematic approach to the Evaluation of the Corrosion Load of Archaeological Metal Objects, in W Mourey, and L Robbiola (eds.), *Metal 98, Proceedings of the International Conference on Metals Conservation, Draguignan-Figanieres, France, 27-29 May 1998*, 80-91. London: James and James, Ltd.

Wang, X. and Zhang, Y. 1987. The Synergetic Effect of Ethanolamine and Benzotriazole on the Corrosion Inhibition of Copper, *Proceedings of the 10th International Congress on Metallic Corrosion 7-11, November 1987 Mandras, India, New Delhi* Oxford and IBH Publishing Co, 2799-2806.

Wharton, G. 2000. Personal Communication.

Woodruff, D.P. and Delchar, T.A. 1994. *Modern Techniques of Surface Science.* Cambridge: Cambridge University Press.

Wu, Y-C. 1993. Studies and Development of Inhibitors for Preventing Copper Corrosion, PhD thesis, University of Pensylvania, USA.

Wu, Y-C. Zhang, P., Pickering, H.W. and Allara, D.L. 1993. Effect of KI on Improving

Copper Corrosion Inhibition Efficiency of Benzotriazole in Sulfuric Acid Electrolytes, *Journal of the Electrochemical Society*, **140**(10), 2791-2800.

Ye, X.R., Xin, X.Q., Zhu, J.J. and Xue, Z.L. 1998. Coordination Compound Films of 1-Phenyl-5-Mercaptotetrazole on Copper Surface, *Applied Surface Science,* **135,** 307-317.

Zdziennicka, A., Jańczuk, B. and Wójik, W. 1998. Influence of Ethyl Xanthate on the wettability and Surface Free Energy of Synthetic Chalcocite, *Powder Technology,* **95**, 234-239.

Zhang, D-Q., Gao, L-X. and Zhou, G-D. 2003. Synergistic effect of 2-mercapto benzimidazole and KI on copper corrosion inhibition in aerated sulfuric acid solution. Journal of Applied Electrochemistry, Vol **33**(5), 361-366.

Zucchi, F., Fonsati, M. and Trabanelli, G. 1998. Influence of the Heat Exchange on the Inhibiting efficiency of some Heterocyclic Derivatives Against Copper Corrosion in 3.5% NaCl Solutions, *Corrosion Science,* Vol **40**(11), 1927-1937.

Zucchi, F., Trabanelli, G. and Monticelli, C. 1996. The Inhibition of Copper Corrosion in 0.1 M NaCl Under Heat Exhange Conditions, *Corrosion Science,* **38**(1), 147-154.

SYNERGISTIC EFFECTS OF ADDITIVES TO BENZOTRIAZOLE SOLUTIONS APPLIED AS CORROSION INHIBITORS TO ARCHAEOLOGICAL COPPER AND COPPER ALLOY ARTEFACTS

Vol. II-Appendices

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Appendix 1

BTA 1	Weight change % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M, 1h	0.0042	0.0046	0.0057	0.0063	0.0070	47.0	44.4	34.1	31.1	27.4
BTA 0.1M, 1h	0.0041	0.0046	0.0060	0.0068	0.0074	48.3	44.4	29.9	25.6	22.5
BTA 0.1M, 1h	0.0039	0.0042	0.0053	0.0062	0.0067	50.1	49.0	38.3	32.8	30.7
BTA 0.1M, 1h	0.0034	0.0040	0.0052	0.0056	0.0064	56.9	51.5	40.1	38.7	33.0
BTA 0.1M, 1h	0.0045	0.0054	0.0056	0.0075	0.0081	43.0	35.0	34.4	18.2	15.6
BTA 0.1M, 24h	0.0058	0.0066	0.0075	0.0083	0.0089	26.0	20.3	12.7	9.7	7.8
BTA 0.1M, 24h	0.0052	0.0061	0.0071	0.0081	0.0088	34.1	27.0	17.0	11.8	8.7
BTA 0.1M, 24h	0.0060	0.0063	0.0072	0.0080	0.0086	24.6	23.7	16.2	12.7	10.2
BTA 0.1M, 24h	0.0065	0.0068	0.0070	0.0090	0.0096	17.6	18.6	18.3	2.2	0.5
BTA 0.1M, 24h	0.0052	0.0058	0.0069	0.0077	0.0084	34.5	29.6	19.9	16.0	12.9
BTA 0.25M, 1h	0.0033	0.0040	0.0051	0.0058	0.0063	58.0	52.0	40.5	37.2	33.9
BTA 0.25M, 1h	0.0031	0.0038	0.0050	0.0057	0.0063	61.3	54.7	42.3	37.6	34.2
BTA 0.25M, 1h	0.0029	0.0035	0.0046	0.0051	0.0057	63.8	58.4	47.1	44.3	40.4
BTA 0.25M, 1h	0.0034	0.0042	0.0050	0.0063	0.0068	56.9	49.5	41.3	31.3	28.7
BTA 0.25M, 1h	0.0037	0.0042	0.0054	0.0062	0.0068	52.7	49.5	37.7	32.3	28.9
BTA 0.25M, 24h	0.0037	0.0045	0.0060	0.0069	0.0075	52.7	45.6	29.9	25.4	21.6
BTA 0.25M, 24h	0.0044	0.0056	0.0069	0.0077	0.0084	44.8	32.7	19.3	16.3	13.0
BTA 0.25M, 24h	0.0053	0.0060	0.0068	0.0073	0.0079	32.5	27.9	21.4	20.4	17.8
BTA 0.25M, 24h	0.0048	0.0056	0.0065	0.0072	0.0078	39.6	32.9	24.3	21.8	19.1
BTA 0.25M, 24h	0.0044	0.0051	0.0063	0.0071	0.0077	44.2	38.1	27.2	23.0	19.8

Inhibitive Efficiency calculated using: 0.0079 (24h), 0.0083 (48h), 0.0086 (168h), 0.0092 (504), 0.0096 (840h). Five replicates for each treatment

Fractional Factorial Fit

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Estimated Effects and Coefficients for 24h (coded units)

Term                 Effect      Coef  StDev Coef       T      P
Constant                      0.004390    0.000107   41.07  0.000
Concentr          -0.000980 -0.000490    0.000107   -4.58  0.000
Immersio           0.001480  0.000740    0.000107    6.92  0.000
Concentr*Immersio -0.000240 -0.000120    0.000107   -1.12  0.278

Analysis of Variance for 24h (coded units)

Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00001575  0.00001575  0.00000788  34.47  0.000
2-Way Interactions    1  0.00000029  0.00000029  0.00000029   1.26  0.278
Residual Error       16  0.00000366  0.00000366  0.00000023
  Pure Error         16  0.00000366  0.00000366  0.00000023
Total                19  0.00001970

Estimated Effects and Coefficients for 48h (coded units)

Term                 Effect      Coef  StDev Coef       T      P
Constant                      0.005045    0.000104   48.49  0.000
Concentr          -0.000790 -0.000395    0.000104   -3.80  0.002
Immersio           0.001590  0.000795    0.000104    7.64  0.000
Concentr*Immersio -0.000170 -0.000085    0.000104   -0.82  0.426

Analysis of Variance for 48h (coded units)
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Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001576	0.00001576	0.00000788	36.40	0.000
2-Way Interactions	1	0.00000014	0.00000014	0.00000014	0.67	0.426
Residual Error	16	0.00000346	0.00000346	0.00000022		
Pure Error	16	0.00000346	0.00000346	0.00000022		
Total	19	0.00001937				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
3	0.004500	0.005360	0.000208	-0.000860	-2.07R
20	0.005400	0.004560	0.000208	0.000840	2.02R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006055	0.000068	88.68	0.000
Concentr	-0.000590	-0.000295	0.000068	-4.32	0.001
Immersio	0.001530	0.000765	0.000068	11.20	0.000
Concentr*Immersio	-0.000050	-0.000025	0.000068	-0.37	0.719

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001344	0.00001344	0.00000672	72.09	0.000
2-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.13	0.719
Residual Error	16	0.00000149	0.00000149	0.00000009		
Pure Error	16	0.00000149	0.00000149	0.00000009		
Total	19	0.00001495				

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006940	0.000115	60.32	0.000
Concentr	-0.000820	-0.000410	0.000115	-3.56	0.003
Immersio	0.001580	0.000790	0.000115	6.87	0.000
Concentr*Immersio	-0.000160	-0.000080	0.000115	-0.70	0.497

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001584	0.00001584	0.00000792	29.92	0.000
2-Way Interactions	1	0.00000013	0.00000013	0.00000013	0.48	0.497
Residual Error	16	0.00000424	0.00000424	0.00000026		
Pure Error	16	0.00000424	0.00000424	0.00000026		
Total	19	0.00002021				

Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid
20	0.007500	0.006480	0.000230	0.001020	2.22R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007555	0.000110	68.79	0.000
Concentr	-0.000870	-0.000435	0.000110	-3.96	0.001
Immersio	0.001610	0.000805	0.000110	7.33	0.000
Concentr*Immersio	-0.000130	-0.000065	0.000110	-0.59	0.562

Analysis of Variance for 840h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001674	0.00001674	0.00000837	34.70	0.000
2-Way Interactions	1	0.00000008	0.00000008	0.00000008	0.35	0.562
Residual Error	16	0.00000386	0.00000386	0.00000024		
Pure Error	16	0.00000386	0.00000386	0.00000024		
Total	19	0.00002069				

Unusual Observations for 840h

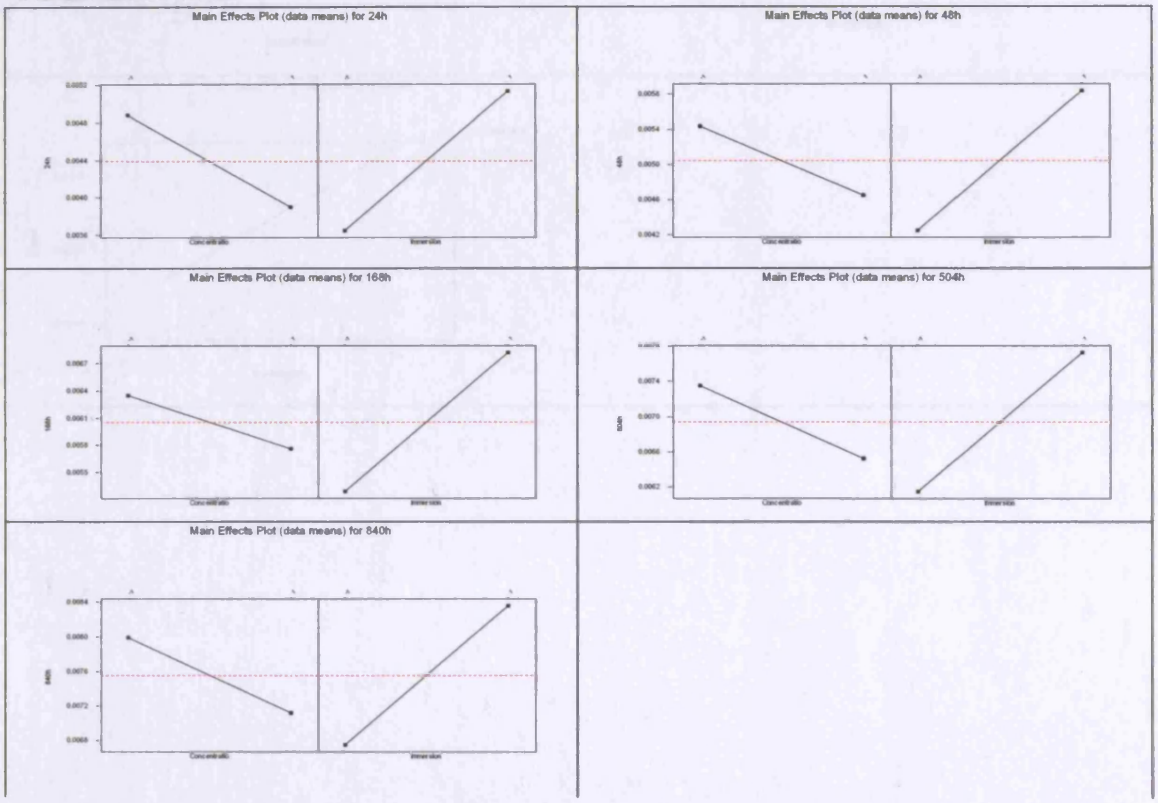
Obs	840h	Fit	StDev Fit	Residual	St Resid
20	0.008100	0.007120	0.000220	0.000980	2.23R

R denotes an observation with a large standardized residual

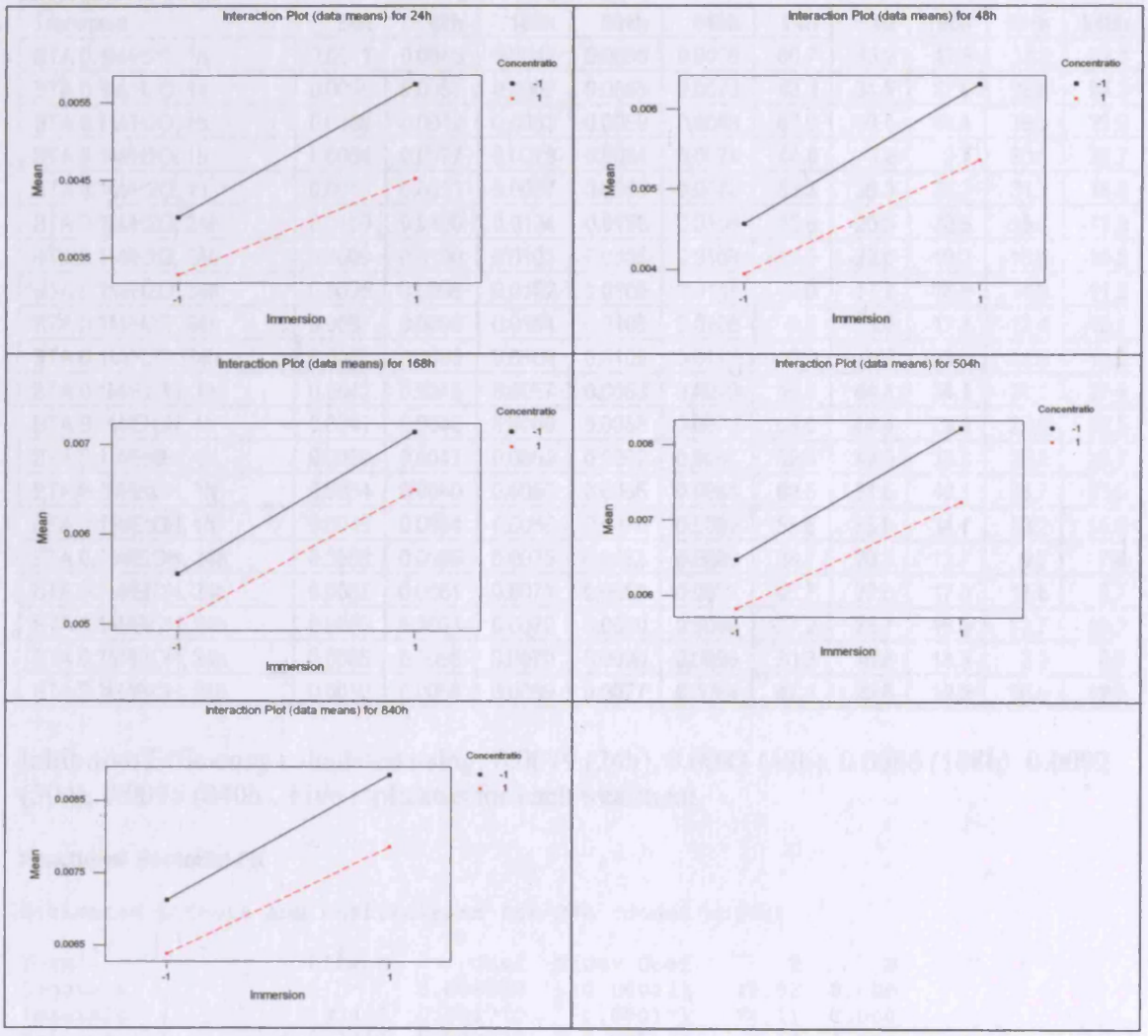
Alias Structure

I
Concentr
Immersion
Concentration*Immersion

Main Effect Plots



Interaction Plots



BTA 2	Weight change % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M/H2O, 1h	0.0041	0.0045	0.0049	0.0056	0.0065	60.7	45.9	42.8	38.9	32.1
BTA 0.1M/H2O, 1h	0.0055	0.0057	0.0062	0.0065	0.0073	43.3	31.9	27.6	28.8	24.3
BTA 0.1M/H2O, 1h	0.0036	0.0042	0.0052	0.0059	0.0068	67.0	49.4	40.1	36.2	29.0
BTA 0.1M/H2O, 1h	0.0054	0.0077	0.0078	0.0064	0.0074	44.8	6.8	9.7	30.9	22.7
BTA 0.1M/H2O, 1h	0.0047	0.0051	0.0057	0.0063	0.0078	53.3	38.3	33.7	31.7	18.8
BTA 0.1M/H2O, 24h	0.0100	0.0100	0.0104	0.0106	0.0108	-13.5	-20.5	-20.5	-15.7	-13.0
BTA 0.1M/H2O, 24h	0.0099	0.0100	0.0103	0.0105	0.0106	-12.3	-20.0	-19.2	-13.6	-10.5
BTA 0.1M/H2O, 24h	0.0096	0.0098	0.0102	0.0105	0.0107	-9.5	-17.7	-18.9	-14.0	-11.2
BTA 0.1M/H2O, 24h	0.0097	0.0099	0.0101	0.0103	0.0106	-9.8	-19.0	-17.3	-12.4	-10.1
BTA 0.1M/H2O, 24h	0.0097	0.0098	0.0106	0.0109	0.0111	-10.0	-18.1	-23.6	-18.5	-15.9
BTA 0.1M/EtOH, 1h	0.0042	0.0046	0.0057	0.0063	0.0070	59.7	44.4	34.1	31.1	27.4
BTA 0.1M/EtOH, 1h	0.0041	0.0046	0.0060	0.0068	0.0074	61.0	44.4	29.9	25.6	22.5
BTA 0.1M/EtOH, 1h	0.0039	0.0042	0.0053	0.0062	0.0067	62.8	49.0	38.3	32.8	30.7
BTA 0.1M/EtOH, 1h	0.0034	0.0040	0.0052	0.0056	0.0064	69.5	51.5	40.1	38.7	33.0
BTA 0.1M/EtOH, 1h	0.0045	0.0054	0.0056	0.0075	0.0081	55.6	35.0	34.4	18.2	15.6
BTA 0.1M/EtOH, 24h	0.0058	0.0066	0.0075	0.0083	0.0089	38.7	20.3	12.7	9.7	7.8
BTA 0.1M/EtOH, 24h	0.0052	0.0061	0.0071	0.0081	0.0088	46.7	27.0	17.0	11.8	8.7
BTA 0.1M/EtOH, 24h	0.0060	0.0063	0.0072	0.0080	0.0086	37.2	23.7	16.2	12.7	10.2
BTA 0.1M/EtOH, 24h	0.0065	0.0068	0.0070	0.0090	0.0096	30.2	18.6	18.3	2.2	0.5
BTA 0.1M/EtOH, 24h	0.0052	0.0058	0.0069	0.0077	0.0084	47.1	29.6	19.9	16.0	12.9

Inhibitive Efficiency calculated using: 0.0079 (24h), 0.0083 (48h), 0.0086 (168h), 0.0092 (504), 0.0096 (840h). Five replicates for each treatment

Fractional Factorial Fit

```
Estimated Effects and Coefficients for 24h (coded units)

Term                 Effect      Coef  StDev Coef       T      P
Constant                      0.006050    0.000121   49.92  0.000
Immersio           0.003420  0.001710    0.000121   14.11  0.000
Solvent           -0.002340 -0.001170    0.000121   -9.65  0.000
Immersio*Solvent  -0.001700 -0.000850    0.000121   -7.01  0.000

Analysis of Variance for 24h (coded units)

Source               DF       Seq SS      Adj SS      Adj MS       F      P
Main Effects          2  0.00008586 0.00008586 0.00004293  146.14  0.000
2-Way Interactions    1  0.00001445 0.00001445 0.00001445   49.19  0.000
Residual Error       16  0.00000470 0.00000470 0.00000029
  Pure Error         16  0.00000470 0.00000470 0.00000029
Total                19  0.00010501

Unusual Observations for 24h

Obs        24h        Fit  StDev Fit   Residual   St Resid
  7   0.003600   0.004660   0.000242  -0.001060      -2.19R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)
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Term	Effect	Coef	StDev Coef	T	P
Constant		0.006555	0.000173	37.98	0.000
Immersio	0.003110	0.001555	0.000173	9.01	0.000
Solvent	-0.002230	-0.001115	0.000173	-6.46	0.000
Immersio*Solvent	-0.001350	-0.000675	0.000173	-3.91	0.001

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00007323	0.00007323	0.00003661	61.46	0.000
2-Way Interactions	1	0.00000911	0.00000911	0.00000911	15.30	0.001
Residual Error	16	0.00000953	0.00000953	0.00000060		
Pure Error	16	0.00000953	0.00000953	0.00000060		
Total	19	0.00009187				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
10	0.007700	0.005440	0.000345	0.002260	3.27R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007245	0.000137	52.98	0.000
Immersio	0.002970	0.001485	0.000137	10.86	0.000
Solvent	-0.001790	-0.000895	0.000137	-6.54	0.000
Immersio*Solvent	-0.001390	-0.000695	0.000137	-5.08	0.000

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00006012	0.00006013	0.00003006	80.38	0.000
2-Way Interactions	1	0.00000966	0.00000966	0.00000966	25.83	0.000
Residual Error	16	0.00000598	0.00000598	0.00000037		
Pure Error	16	0.00000598	0.00000598	0.00000037		
Total	19	0.00007577				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
10	0.007800	0.005960	0.000273	0.001840	3.36R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007850	0.000108	72.61	0.000
Immersio	0.003080	0.001540	0.000108	14.24	0.000
Solvent	-0.001000	-0.000500	0.000108	-4.62	0.000
Immersio*Solvent	-0.001340	-0.000670	0.000108	-6.20	0.000

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00005243	0.00005243	0.00002622	112.15	0.000
2-Way Interactions	1	0.00000898	0.00000898	0.00000898	38.41	0.000
Residual Error	16	0.00000374	0.00000374	0.00000023		
Pure Error	16	0.00000374	0.00000374	0.00000023		
Total	19	0.00006515				

Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid
15	0.005600	0.006480	0.000216	-0.000880	-2.03R
16	0.007500	0.006480	0.000216	0.001020	2.36R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008475	0.000109	77.73	0.000
Immersio	0.002670	0.001335	0.000109	12.24	0.000
Solvent	-0.000970	-0.000485	0.000109	-4.45	0.000
Immersio*Solvent	-0.000930	-0.000465	0.000109	-4.26	0.001

Analysis of Variance for 840h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00004035	0.00004035	0.00002017	84.86	0.000
2-Way Interactions	1	0.00000432	0.00000432	0.00000432	18.19	0.001
Residual Error	16	0.00000380	0.00000380	0.00000024		
Pure Error	16	0.00000380	0.00000380	0.00000024		
Total	19	0.00004848				

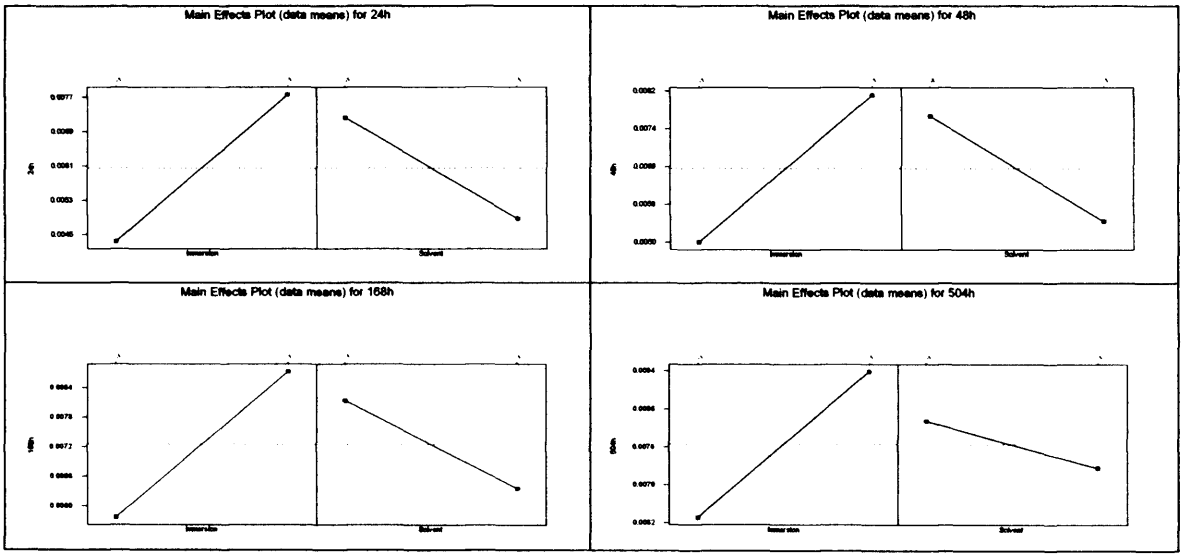
Unusual Observations for 840h

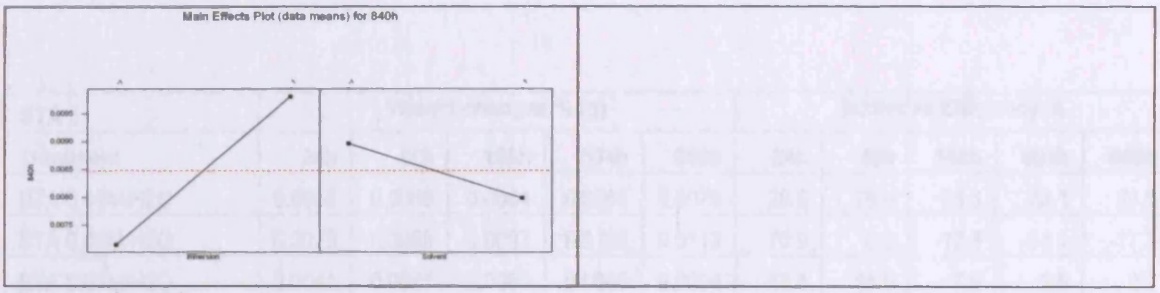
Obs	840h	Fit	StDev Fit	Residual	St Resid
16	0.008100	0.007120	0.000218	0.000980	2.25R

R denotes an observation with a large standardized residual

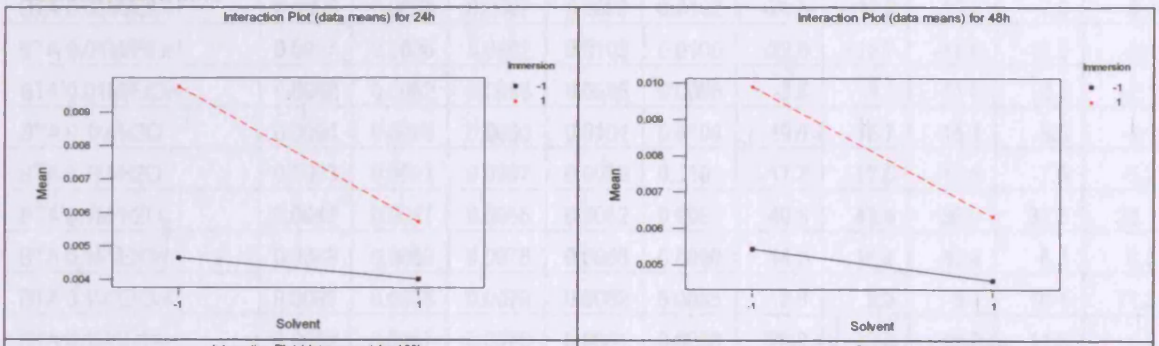
Alias Structure
I
Immersion
Solvent
Immersion*Solvent

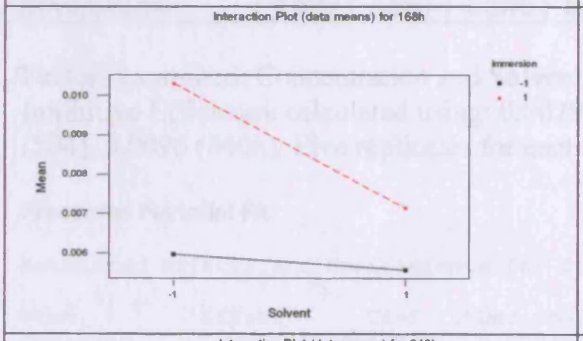
Main Effect Plots

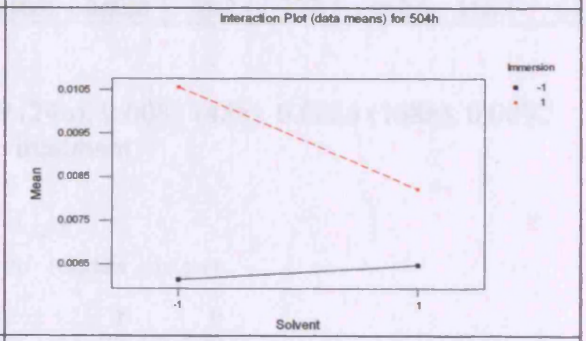


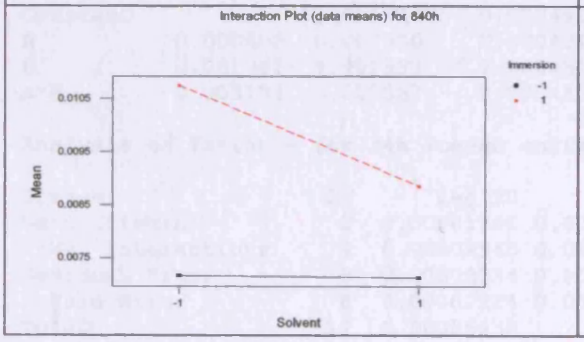


Interaction Plots









BTA 3	Weight changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.01M/H2O	0.0058	0.0059	0.0064	0.0068	0.0075	26.6	28.9	25.6	26.1	21.9
BTA 0.01M/H2O	0.0023	0.0083	0.0097	0.0105	0.0113	70.9	0.0	-12.8	-14.1	-17.7
BTA 0.01M/H2O	0.0041	0.0071	0.0080	0.0086	0.0094	48.1	14.5	7.0	6.5	2.1
BTA 0.01M/EtOH	0.0096	0.0093	0.0097	0.0099	0.0102	-21.5	-12.0	-12.8	-7.6	-6.3
BTA 0.01M/EtOH	0.0097	0.0096	0.0102	0.0103	0.0105	-22.8	-15.7	-18.6	-12.0	-9.4
BTA 0.01M/EtOH	0.0082	0.0082	0.0096	0.0095	0.0098	-3.8	1.2	-11.6	-3.3	-2.1
BTA 0.1M/H2O	0.0094	0.0096	0.0099	0.0101	0.0104	-19.0	-15.7	-15.1	-9.8	-8.3
BTA 0.1M/H2O	0.0093	0.0093	0.0097	0.0099	0.0101	-17.7	-12.0	-12.8	-7.6	-5.2
BTA 0.1M/H2O	0.0047	0.0047	0.0055	0.0062	0.0069	40.5	43.4	36.0	32.6	28.1
BTA 0.1M/EtOH	0.0068	0.0069	0.0075	0.0086	0.0090	14.2	16.4	12.4	6.3	6.3
BTA 0.1M/EtOH	0.0069	0.0075	0.0078	0.0082	0.0085	12.9	9.2	9.1	10.4	11.2
BTA 0.1M/EtOH	0.0062	0.0067	0.0070	0.0081	0.0088	20.9	19.0	18.8	11.6	8.2

Factors examined: Concentration and Solvent
Inhibitive Efficiency calculated using: 0.0079 (24h), 0.0083 (48h), 0.0086 (168h), 0.0092 (504), 0.0096 (840h). Five replicates for each treatment

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006917	0.000481	14.37	0.000
A	0.000600	0.000300	0.000481	0.62	0.550
B	0.001967	0.000983	0.000481	2.04	0.075
A*B	-0.003133	-0.001567	0.000481	-3.25	0.012

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001268	0.00001268	0.00000634	2.28	0.164
2-Way Interactions	1	0.00002945	0.00002945	0.00002945	10.59	0.012
Residual Error	8	0.00002224	0.00002224	0.00000278		
Pure Error	8	0.00002224	0.00002224	0.00000278		
Total	11	0.00006438				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
11	0.004700	0.007800	0.000963	-0.003100	-2.28R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007758	0.000450	17.26	0.000
A	-0.000617	-0.000308	0.000450	-0.69	0.512

B	0.000550	0.000275	0.000450	0.61	0.558
A*B	-0.001383	-0.000692	0.000450	-1.54	0.162

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000205	0.00000205	0.00000102	0.42	0.669
2-Way Interactions	1	0.00000574	0.00000574	0.00000574	2.37	0.162
Residual Error	8	0.00001940	0.00001940	0.00000243		
Pure Error	8	0.00001940	0.00001940	0.00000243		
Total	11	0.00002719				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
11	0.004700	0.007867	0.000899	-0.003167	-2.49R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008417	0.000437	19.26	0.000
A	-0.001033	-0.000517	0.000437	-1.18	0.271
B	0.000433	0.000217	0.000437	0.50	0.633
A*B	-0.001367	-0.000683	0.000437	-1.56	0.156

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000377	0.00000377	0.00000188	0.82	0.473
2-Way Interactions	1	0.00000560	0.00000560	0.00000560	2.45	0.156
Residual Error	8	0.00001833	0.00001833	0.00000229		
Pure Error	8	0.00001833	0.00001833	0.00000229		
Total	11	0.00002770				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
11	0.005500	0.008367	0.000874	-0.002867	-2.32R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008892	0.000420	21.16	0.000
A	-0.000750	-0.000375	0.000420	-0.89	0.398
B	0.000417	0.000208	0.000420	0.50	0.633
A*B	-0.000850	-0.000425	0.000420	-1.01	0.341

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000221	0.00000221	0.00000110	0.52	0.613
2-Way Interactions	1	0.00000217	0.00000217	0.00000217	1.02	0.341
Residual Error	8	0.00001695	0.00001695	0.00000212		
Pure Error	8	0.00001695	0.00001695	0.00000212		
Total	11	0.00002133				

Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid

```
 11    0.006200    0.008733    0.000840  -0.002533      -2.13R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840h (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant              0.009367    0.000397   23.60  0.000
A         -0.000833 -0.000417    0.000397   -1.05  0.324
B          0.000200  0.000100    0.000397    0.25  0.807
A*B       -0.000567 -0.000283    0.000397   -0.71  0.496

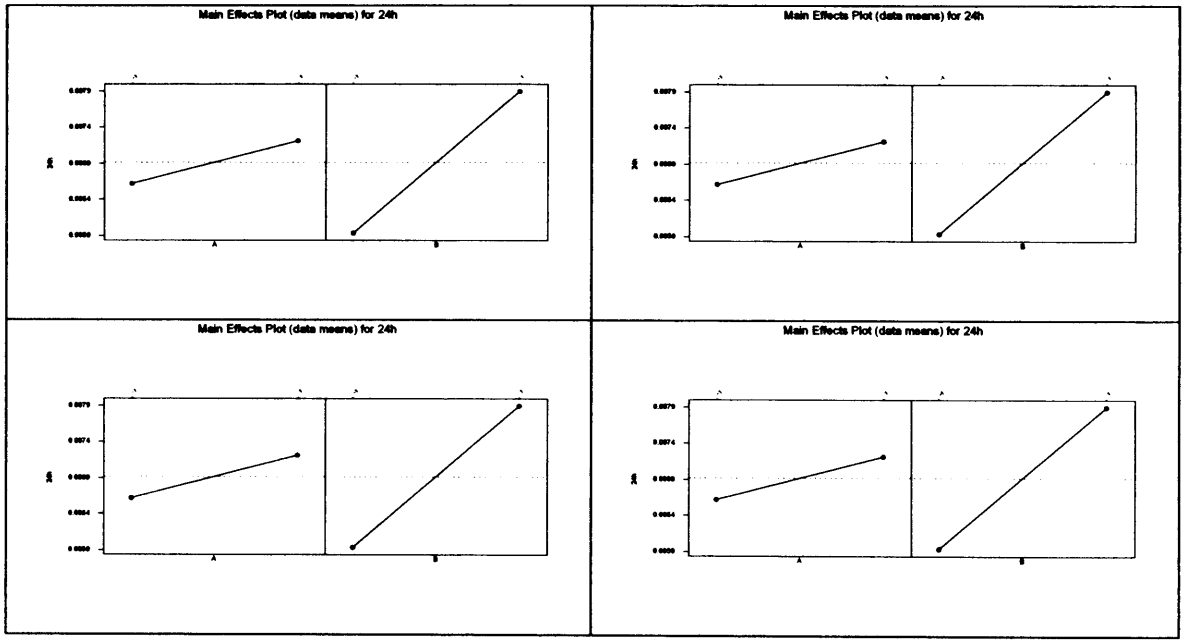
Analysis of Variance for 840h (coded units)

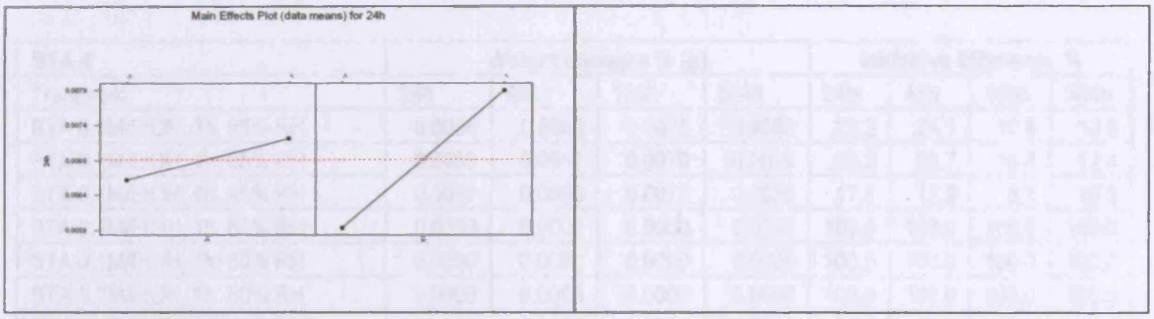
Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00000220 0.00000220 0.00000110   0.58  0.580
2-Way Interactions    1  0.00000096 0.00000096 0.00000096   0.51  0.496
Residual Error        8  0.00001512 0.00001512 0.00000189
  Pure Error          8  0.00001512 0.00001512 0.00000189
Total                11  0.00001829

Alias Structure

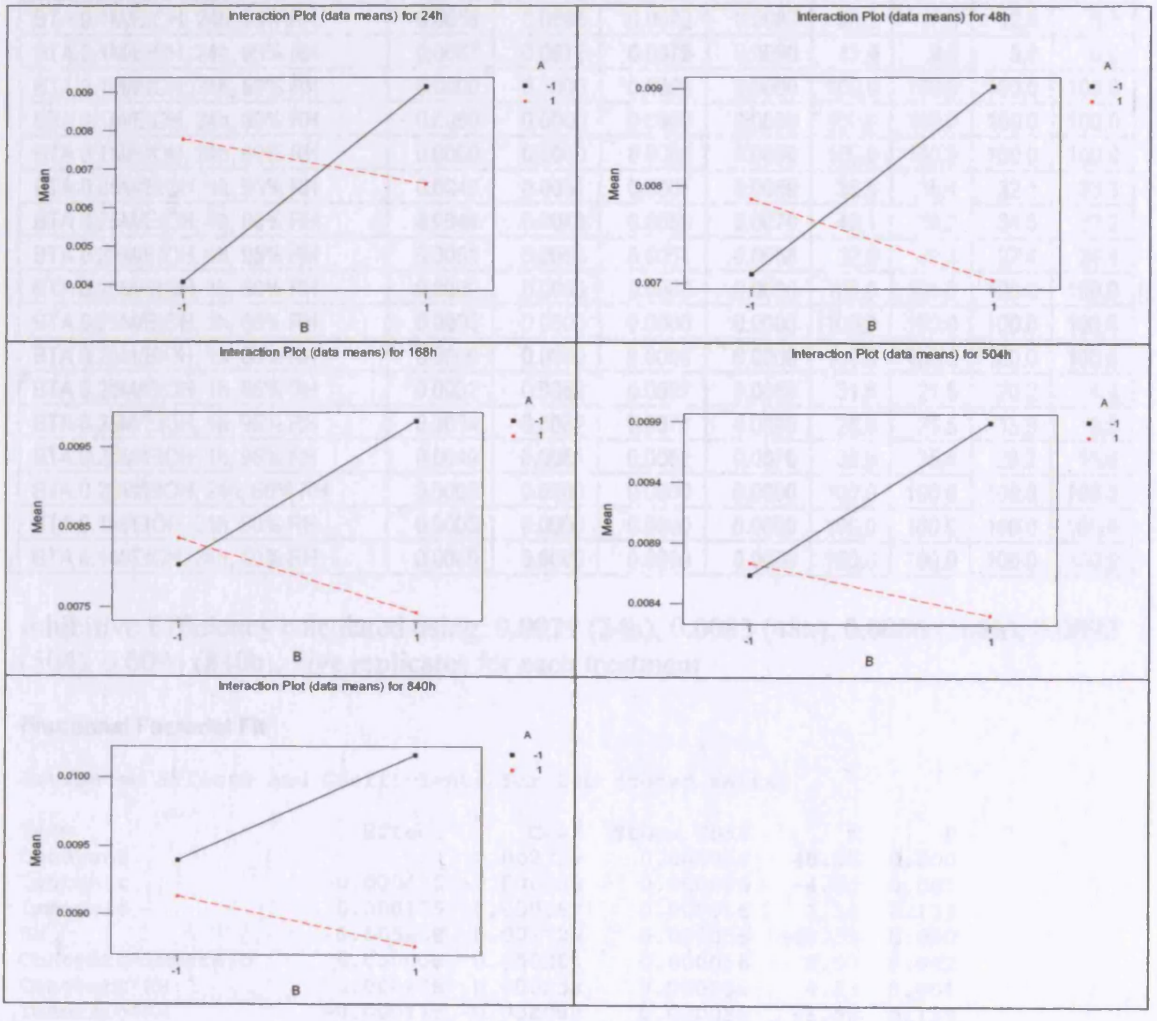
I
A
B
A*B
```

Main Effect Plots





Interaction Plots



BTA 4	Weight changes % (g)				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M/EtOH, 1h, 95% RH	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M/EtOH, 1h, 95% RH	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M/EtOH, 1h, 95% RH	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 95% RH	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M/EtOH, 24h, 95% RH	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M/EtOH, 24h, 95% RH	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 95% RH	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M/EtOH, 1h, 95% RH	0.0044	0.0048	0.0055	0.0070	42.1	39.2	34.5	22.2
BTA 0.25M/EtOH, 1h, 95% RH	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.25M/EtOH, 1h, 95% RH	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M/EtOH, 1h, 95% RH	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M/EtOH, 1h, 95% RH	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0
BTA 0.1M/EtOH, 24h, 60% RH	0.0000	0.0000	0.0000	0.0000	100.0	100.0	100.0	100.0

Inhibitive Efficiency calculated using: 0.0079 (24h), 0.0083 (48h), 0.0086 (168h), 0.0092 (504), 0.0096 (840h). Five replicates for each treatment

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.002729	0.000056	48.55	0.000
Concentr	-0.000475	-0.000238	0.000056	-4.23	0.001
Immersio	0.000175	0.000087	0.000056	1.56	0.139
RH	-0.005458	-0.002729	0.000056	-48.55	0.000
Concentr*Immersio	0.000008	0.000004	0.000056	0.07	0.942
Concentr*RH	0.000475	0.000238	0.000056	4.23	0.001
Immersio*RH	-0.000175	-0.000088	0.000056	-1.56	0.139
Concentr*Immersio*RH	-0.000008	-0.000004	0.000056	-0.07	0.942

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00018030	0.00018030	0.00006010	792.52	0.000
2-Way Interactions	3	0.00000154	0.00000154	0.00000051	6.76	0.004
3-Way Interactions	1	0.00000000	0.00000000	0.00000000	0.01	0.942
Residual Error	16	0.00000121	0.00000121	0.00000008		
Pure Error	16	0.00000121	0.00000121	0.00000008		

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Total                 23  0.00018305

Unusual Observations for 24h

Obs        24h        Fit  StDev Fit   Residual   St Resid
 21   0.006700   0.006100   0.000159   0.000600       2.67R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term                     Effect      Coef  StDev Coef       T      P
Constant                          0.003008    0.000069   43.62  0.000
Concentr               -0.000533 -0.000267    0.000069   -3.87  0.001
Immersio                0.000283  0.000142    0.000069    2.05  0.057
RH                     -0.006017 -0.003008    0.000069  -43.62  0.000
Concentr*Immersio       0.000067  0.000033    0.000069    0.48  0.635
Concentr*RH             0.000533  0.000267    0.000069    3.87  0.001
Immersio*RH            -0.000283 -0.000142    0.000069   -2.05  0.057
Concentr*Immersio*RH   -0.000067 -0.000033    0.000069   -0.48  0.635

Analysis of Variance for 48h (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           3  0.00021939  0.00021939  0.00007313 640.55  0.000
2-Way Interactions     3  0.00000222  0.00000222  0.00000074   6.47  0.004
3-Way Interactions     1  0.00000003  0.00000003  0.00000003   0.23  0.635
Residual Error        16  0.00000183  0.00000183  0.00000011
  Pure Error          16  0.00000183  0.00000183  0.00000011
Total                 23  0.00022346

Unusual Observations for 48h

Obs        48h        Fit  StDev Fit   Residual   St Resid
 15   0.005100   0.005833   0.000195  -0.000733      -2.66R
 24   0.006900   0.006333   0.000195   0.000567       2.05R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term                     Effect      Coef  StDev Coef       T      P
Constant                          0.003421    0.000053   65.11  0.000
Concentr               -0.000625 -0.000313    0.000053   -5.95  0.000
Immersio                0.000258  0.000129    0.000053    2.46  0.026
RH                     -0.006842 -0.003421    0.000053  -65.11  0.000
Concentr*Immersio       0.000192  0.000096    0.000053    1.82  0.087
Concentr*RH             0.000625  0.000313    0.000053    5.95  0.000
Immersio*RH            -0.000258 -0.000129    0.000053   -2.46  0.026
Concentr*Immersio*RH   -0.000192 -0.000096    0.000053   -1.82  0.087

Analysis of Variance for 168h (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           3  0.00028359  0.00028359  0.00009453  1E+03  0.000
2-Way Interactions     3  0.00000296  0.00000296  0.00000099  14.92  0.000
3-Way Interactions     1  0.00000022  0.00000022  0.00000022   3.33  0.087
Residual Error        16  0.00000106  0.00000106  0.00000007
  Pure Error          16  0.00000106  0.00000106  0.00000007
Total                 23  0.00028784

Unusual Observations for 168h
```

Obs	168h	Fit	StDev Fit	Residual	St Resid
6	0.007100	0.006667	0.000149	0.000433	2.06R
15	0.006200	0.006667	0.000149	-0.000467	-2.22R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.003979	0.000044	89.44	0.000
Concentr	-0.000392	-0.000196	0.000044	-4.40	0.000
Immersio	0.000525	0.000262	0.000044	5.90	0.000
RH	-0.007958	-0.003979	0.000044	-89.44	0.000
Concentr*Immersio	0.000142	0.000071	0.000044	1.59	0.131
Concentr*RH	0.000392	0.000196	0.000044	4.40	0.000
Immersio*RH	-0.000525	-0.000263	0.000044	-5.90	0.000
Concentr*Immersio*RH	-0.000142	-0.000071	0.000044	-1.59	0.131

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00038258	0.00038258	0.00012753	3E+03	0.000
2-Way Interactions	3	0.00000269	0.00000269	0.00000090	18.91	0.000
3-Way Interactions	1	0.00000012	0.00000012	0.00000012	2.54	0.131
Residual Error	16	0.00000076	0.00000076	0.00000005		
Pure Error	16	0.00000076	0.00000076	0.00000005		
Total	23	0.00038616				

Unusual Observations for 504h

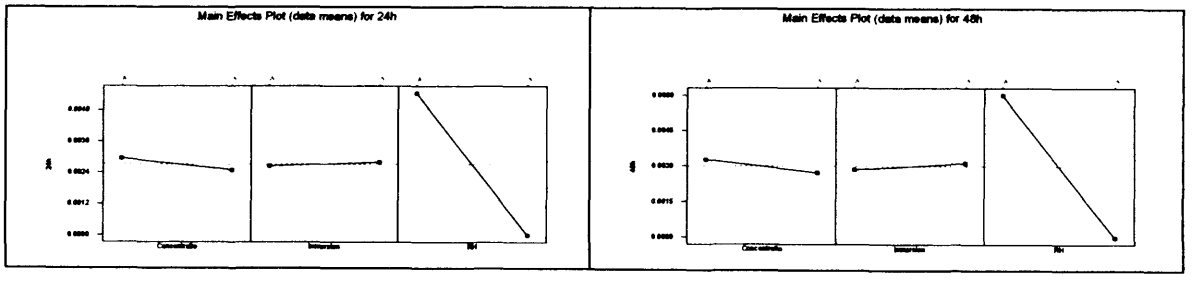
Obs	504h	Fit	StDev Fit	Residual	St Resid
1	0.008600	0.008233	0.000126	0.000367	2.06R
15	0.007600	0.008233	0.000126	-0.000633	-3.56R

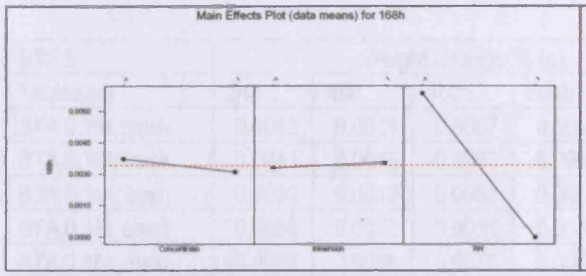
R denotes an observation with a large standardized residual

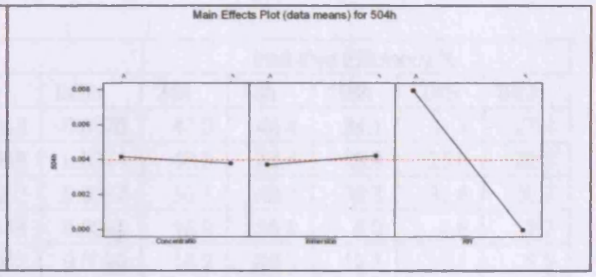
Alias Structure

I
Concentr
Immersio
RH
Concentr*Immersio
Concentr*RH
Immersio*RH
Concentr*Immersio*RH

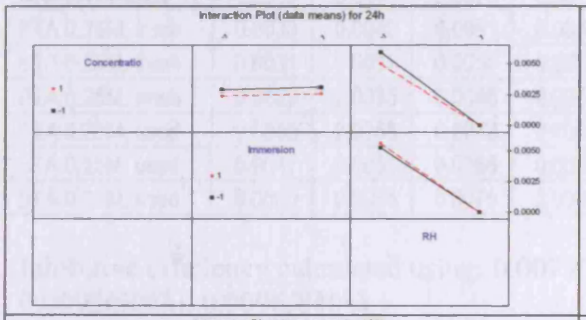
Main Effect Plots

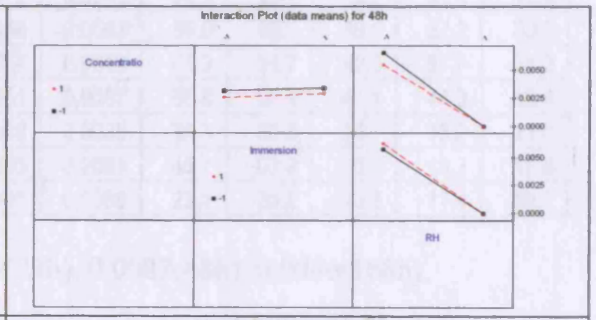


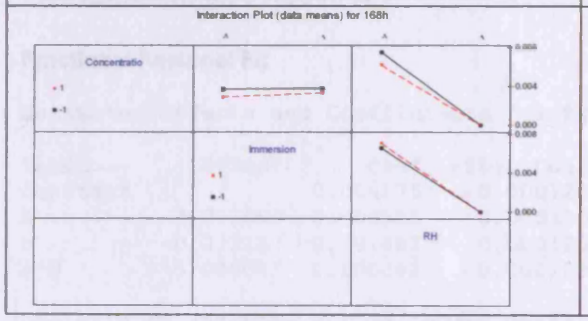


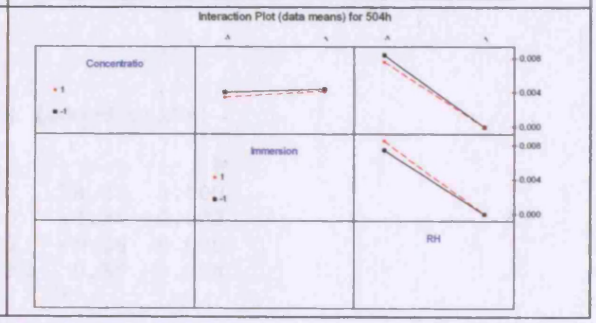


Interaction Plots









BTA 5	Weight Change % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M, fresh	0.0042	0.0046	0.0057	0.0063	0.0070	47.0	44.4	34.1	31.1	27.4
BTA 0.1M, fresh	0.0041	0.0046	0.0060	0.0068	0.0074	48.3	44.4	29.9	25.6	22.5
BTA 0.1M, fresh	0.0039	0.0042	0.0053	0.0062	0.0067	50.1	49.0	38.3	32.8	30.7
BTA 0.1M, used	0.0066	0.0070	0.0081	0.0088	0.0093	16.9	15.8	6.0	4.6	2.7
BTA 0.1M, used	0.0065	0.0068	0.0076	0.0082	0.0090	18.2	18.5	12.1	11.1	6.2
BTA 0.1M, used	0.0059	0.0063	0.0075	0.0072	0.0079	24.8	23.9	13.0	22.1	17.2
BTA 0.25M, fresh	0.0033	0.0040	0.0051	0.0058	0.0063	58.0	52.0	40.5	37.2	33.9
BTA 0.25M, fresh	0.0031	0.0038	0.0050	0.0057	0.0063	61.3	54.7	42.3	37.6	34.2
BTA 0.25M, fresh	0.0029	0.0035	0.0046	0.0051	0.0057	63.8	58.4	47.1	44.3	40.4
BTA 0.25M, used	0.0049	0.0058	0.0073	0.0080	0.0085	38.3	30.5	14.7	13.3	11.0
BTA 0.25M, used	0.0047	0.0055	0.0068	0.0075	0.0081	40.7	33.2	20.5	18.2	15.6
BTA 0.25M, used	0.0060	0.0066	0.0075	0.0081	0.0086	23.4	20.2	13.1	11.4	10.2

Inhibitive efficiency calculated using: 0.0079(24h), 0.0083(48h), 0.0086(168h), 0.0092(504h), 0.0096(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.004675	0.000120	38.81	0.000
A	-0.001050	-0.000525	0.000120	-4.36	0.002
B	-0.002183	-0.001092	0.000120	-9.06	0.000
A*B	0.000083	0.000042	0.000120	0.35	0.738

Analysis of Variance for 24 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001761	0.00001761	0.00000880	50.55	0.000
2-Way Interactions	1	0.00000002	0.00000002	0.00000002	0.12	0.738
Residual Error	8	0.00000139	0.00000139	0.00000017		
Pure Error	8	0.00000139	0.00000139	0.00000017		
Total	11	0.00001902				

Unusual Observations for 24

Obs	24	Fit	StDev Fit	Residual	St Resid
12	0.006000	0.005200	0.000241	0.000800	2.35R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.005225	0.000109	47.95	0.000
A	-0.000717	-0.000358	0.000109	-3.29	0.011
B	-0.002217	-0.001108	0.000109	-10.17	0.000
A*B	0.000017	0.000008	0.000109	0.08	0.941

Analysis of Variance for 48 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001628	0.00001628	0.00000814	57.13	0.000

2-Way Interactions	1	0.00000000	0.00000000	0.00000000	0.01	0.941
Residual Error	8	0.00000114	0.00000114	0.00000014		
Pure Error	8	0.00000114	0.00000114	0.00000014		
Total	11	0.00001742				

Unusual Observations for 48

Obs	48	Fit	StDev Fit	Residual	St Resid
12	0.006600	0.005967	0.000218	0.000633	2.05R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006375	0.000094	67.62	0.000
A	-0.000650	-0.000325	0.000094	-3.45	0.009
B	-0.002183	-0.001092	0.000094	-11.58	0.000
A*B	-0.000117	-0.000058	0.000094	-0.62	0.553

Analysis of Variance for 168 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001557	0.00001557	0.00000778	72.98	0.000
2-Way Interactions	1	0.00000004	0.00000004	0.00000004	0.38	0.553
Residual Error	8	0.00000085	0.00000085	0.00000011		
Pure Error	8	0.00000085	0.00000085	0.00000011		
Total	11	0.00001646				

Estimated Effects and Coefficients for 504 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006975	0.000145	48.24	0.000
A	-0.000550	-0.000275	0.000145	-1.90	0.094
B	-0.001983	-0.000992	0.000145	-6.86	0.000
A*B	-0.000350	-0.000175	0.000145	-1.21	0.261

Analysis of Variance for 504 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001271	0.00001271	0.00000635	25.33	0.000
2-Way Interactions	1	0.00000037	0.00000037	0.00000037	1.47	0.261
Residual Error	8	0.00000201	0.00000201	0.00000025		
Pure Error	8	0.00000201	0.00000201	0.00000025		
Total	11	0.00001508				

Unusual Observations for 504

Obs	504	Fit	StDev Fit	Residual	St Resid
10	0.007200	0.008067	0.000289	-0.000867	-2.12R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007567	0.000134	56.64	0.000
A	-0.000633	-0.000317	0.000134	-2.37	0.045
B	-0.002000	-0.001000	0.000134	-7.49	0.000
A*B	-0.000300	-0.000150	0.000134	-1.12	0.294

Analysis of Variance for 840 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001320	0.00001320	0.00000660	30.82	0.000
2-Way Interactions	1	0.00000027	0.00000027	0.00000027	1.26	0.294
Residual Error	8	0.00000171	0.00000171	0.00000021		
Pure Error	8	0.00000171	0.00000171	0.00000021		
Total	11	0.00001519				

Unusual Observations for 840

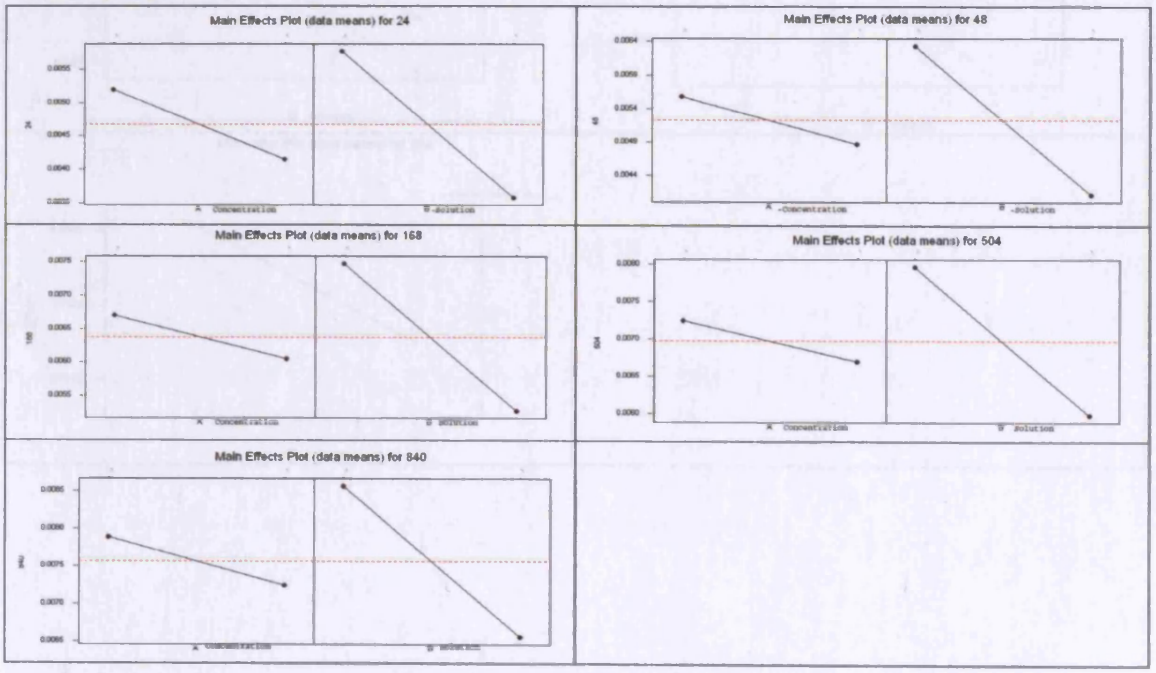
Obs	840	Fit	StDev Fit	Residual	St Resid
10	0.007900	0.008733	0.000267	-0.000833	-2.21R

R denotes an observation with a large standardized residual

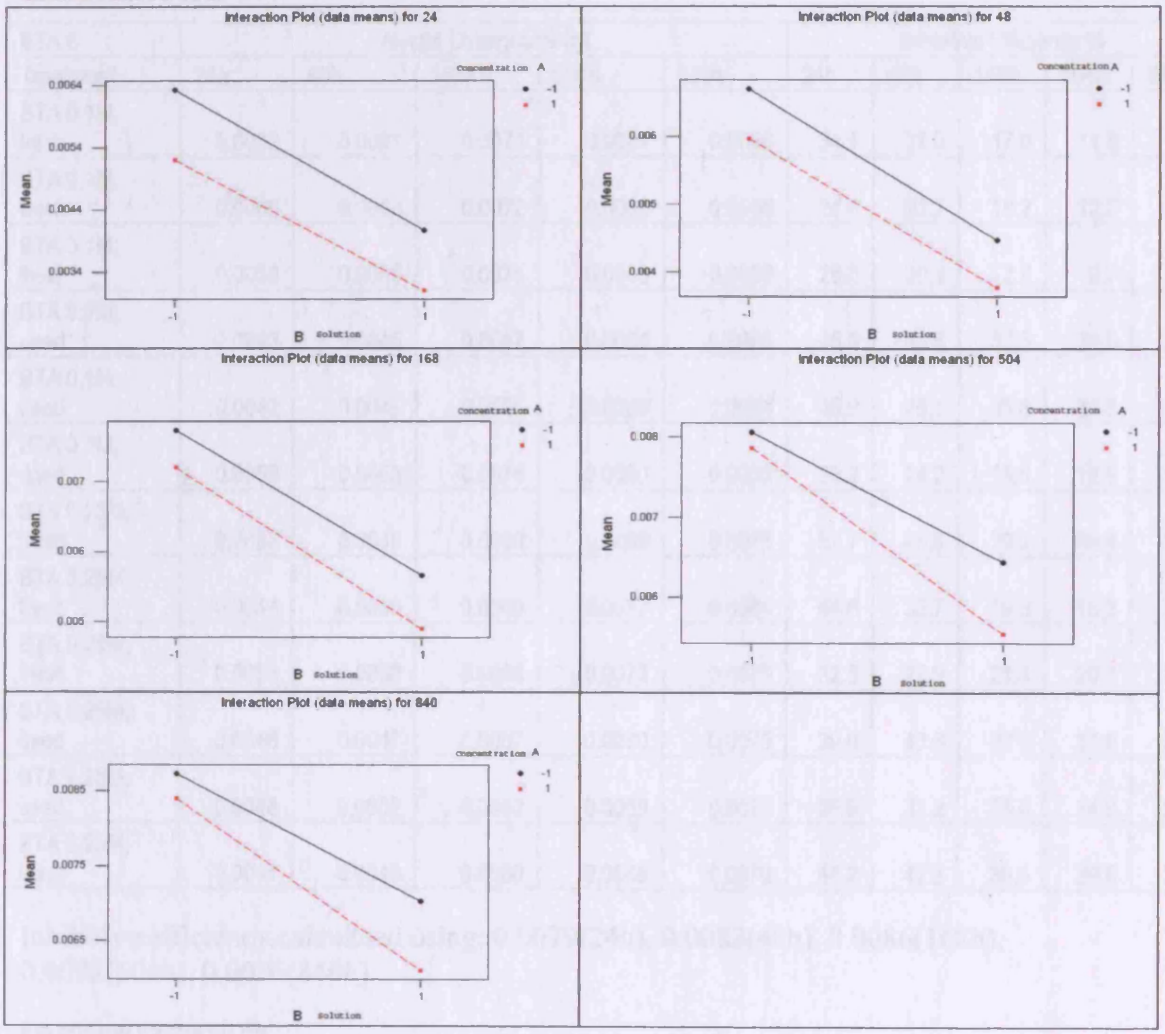
Alias Structure

I
A
B
A*B

Main Effect Plots



Interaction Plots



BTA 6	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M, fresh	0.0052	0.0061	0.0071	0.0081	0.0088	34.1	27.0	17.0	11.8	8.7
BTA 0.1M, fresh	0.0060	0.0063	0.0072	0.0080	0.0086	24.6	23.7	16.2	12.7	10.2
BTA 0.1M, fresh	0.0058	0.0066	0.0075	0.0083	0.0089	26.0	20.3	12.7	9.7	7.8
BTA 0.1M, used	0.0043	0.0045	0.0057	0.0064	0.0069	45.9	45.5	33.3	30.6	28.2
BTA 0.1M, used	0.0042	0.0045	0.0055	0.0058	0.0063	46.9	46.1	35.6	36.8	34.0
BTA 0.1M, used	0.0059	0.0063	0.0074	0.0080	0.0085	25.2	24.2	13.5	12.6	11.1
BTA 0.25M, fresh	0.0037	0.0045	0.0060	0.0069	0.0075	52.7	45.6	29.9	25.4	21.6
BTA 0.25M, fresh	0.0044	0.0056	0.0069	0.0077	0.0084	44.8	32.7	19.3	16.3	13.0
BTA 0.25M, fresh	0.0053	0.0060	0.0068	0.0073	0.0079	32.5	27.9	21.4	20.4	17.8
BTA 0.25M, used	0.0048	0.0047	0.0067	0.0070	0.0075	39.0	43.6	22.3	23.6	22.1
BTA 0.25M, used	0.0048	0.0052	0.0062	0.0069	0.0074	39.6	37.2	28.4	24.9	22.9
BTA 0.25M, used	0.0044	0.0048	0.0060	0.0065	0.0070	44.2	42.3	30.5	29.6	27.1

Inhibitive efficiency calculated using: 0.0079(24h), 0.0083(48h), 0.0086(168h), 0.0092(504h), 0.0096(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.004750	0.000146	32.58	0.000
A	-0.000533	-0.000267	0.000146	-1.83	0.105
B	-0.000233	-0.000117	0.000146	-0.80	0.447
A*B	-0.000133	-0.000067	0.000146	-0.46	0.660

Analysis of Variance for 24 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000102	0.00000102	0.00000051	1.99	0.198
2-Way Interactions	1	0.00000005	0.00000005	0.00000005	0.21	0.660
Residual Error	8	0.00000204	0.00000204	0.00000026		
Pure Error	8	0.00000204	0.00000204	0.00000026		
Total	11	0.00000311				

Estimated Effects and Coefficients for 48 (coded units)

Term	Effect	Coef	StDev Coef	T	P

Constant		0.005200	0.000144	36.21	0.000
A	-0.000433	-0.000217	0.000144	-1.51	0.170
B	0.000433	0.000217	0.000144	1.51	0.170
A*B	-0.000267	-0.000133	0.000144	-0.93	0.380

Analysis of Variance for 48 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000113	0.00000113	0.00000056	2.28	0.165
2-Way Interactions	1	0.00000021	0.00000021	0.00000021	0.86	0.380
Residual Error	8	0.00000198	0.00000198	0.00000025		
Pure Error	8	0.00000198	0.00000198	0.00000025		
Total	11	0.00000332				

Estimated Effects and Coefficients for 168 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006475	0.000146	44.20	0.000
A	-0.000383	-0.000192	0.000146	-1.31	0.227
B	0.000283	0.000142	0.000146	0.97	0.362
A*B	-0.000317	-0.000158	0.000146	-1.08	0.311

Analysis of Variance for 168 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000068	0.00000068	0.00000034	1.32	0.319
2-Way Interactions	1	0.00000030	0.00000030	0.00000030	1.17	0.311
Residual Error	8	0.00000206	0.00000206	0.00000026		
Pure Error	8	0.00000206	0.00000206	0.00000026		
Total	11	0.00000304				

Unusual Observations for 168

Obs	168	Fit	StDev Fit	Residual	St Resid
3	0.007400	0.006367	0.000293	0.001033	2.49R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007258	0.000105	69.29	0.000
A	-0.000650	-0.000325	0.000105	-3.10	0.015
B	0.000417	0.000208	0.000105	1.99	0.082
A*B	-0.000150	-0.000075	0.000105	-0.72	0.494

Analysis of Variance for 504 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000179	0.00000179	0.00000089	6.79	0.019
2-Way Interactions	1	0.00000007	0.00000007	0.00000007	0.51	0.494
Residual Error	8	0.00000105	0.00000105	0.00000013		
Pure Error	8	0.00000105	0.00000105	0.00000013		
Total	11	0.00000291				

Unusual Observations for 504

Obs	504	Fit	StDev Fit	Residual	St Resid
3	0.008000	0.007300	0.000209	0.000700	2.36R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007775	0.000129	60.22	0.000
A	-0.000583	-0.000292	0.000129	-2.26	0.054
B	0.000683	0.000342	0.000129	2.65	0.029
A*B	-0.000317	-0.000158	0.000129	-1.23	0.255

Analysis of Variance for 840 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000242	0.00000242	0.00000121	6.05	0.025
2-Way Interactions	1	0.00000030	0.00000030	0.00000030	1.50	0.255
Residual Error	8	0.00000160	0.00000160	0.00000020		
Pure Error	8	0.00000160	0.00000160	0.00000020		
Total	11	0.00000432				

Unusual Observations for 840

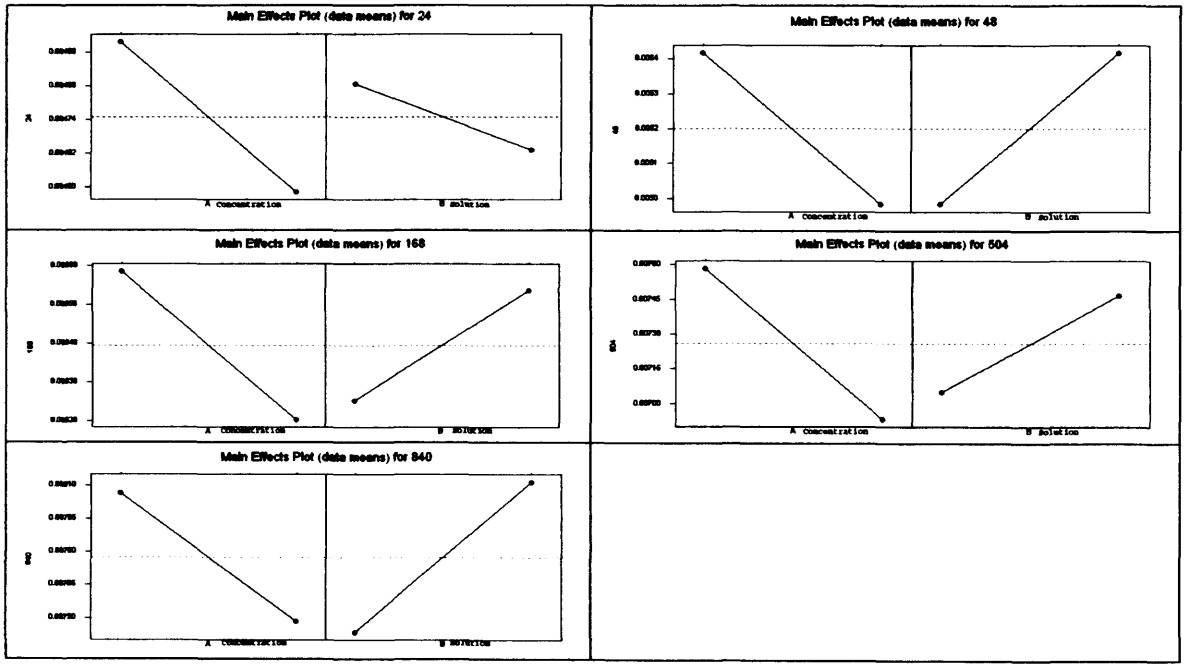
Obs	840	Fit	StDev Fit	Residual	St Resid
3	0.008500	0.007567	0.000258	0.000933	2.56R

R denotes an observation with a large standardized residual

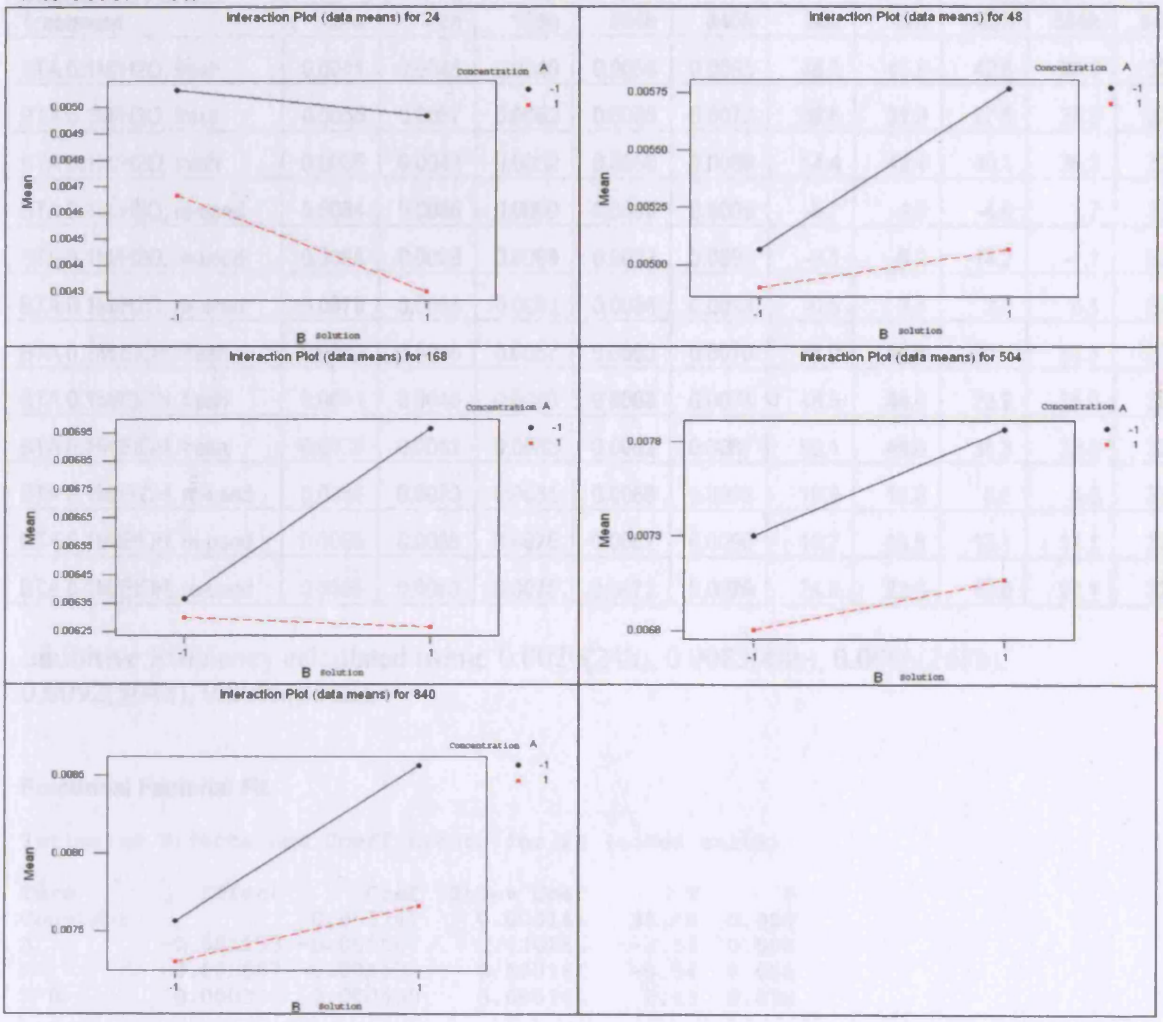
Alias Structure

I
A
B
A*B

Main Effect Plots



Interaction Plots



BTA 7	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M/H2O, fresh	0.0041	0.0045	0.0049	0.0056	0.0065	48.1	45.9	42.8	38.9	32.3
BTA 0.1M/H2O, fresh	0.0055	0.0057	0.0062	0.0065	0.0073	30.6	31.9	27.6	28.8	32.3
BTA 0.1M/H2O, fresh	0.0036	0.0042	0.0052	0.0059	0.0068	54.4	49.4	40.1	36.2	32.3
BTA 0.1M/H2O, re-used	0.0084	0.0086	0.0090	0.0090	0.0099	-6.7	-4.0	-4.6	1.7	32.3
BTA 0.1M/H2O, re-used	0.0085	0.0088	0.0098	0.0093	0.0093	-8.1	-6.2	-14.2	-1.1	32.3
BTA 0.1M/H2O, re-used	0.0079	0.0081	0.0083	0.0086	0.0093	-0.5	2.7	3.0	6.1	32.3
BTA 0.1M/EtOH, fresh	0.0042	0.0046	0.0057	0.0063	0.0070	47.0	44.4	34.1	31.1	32.3
BTA 0.1M/EtOH, fresh	0.0041	0.0046	0.0060	0.0068	0.0074	48.3	44.4	29.9	25.6	32.3
BTA 0.1M/EtOH, fresh	0.0039	0.0042	0.0053	0.0062	0.0067	50.1	49.0	38.3	32.8	32.3
BTA 0.1M/EtOH, re-used	0.0066	0.0070	0.0081	0.0088	0.0093	16.9	15.8	6.0	4.6	32.3
BTA 0.1M/EtOH, re-used	0.0065	0.0068	0.0076	0.0082	0.0090	18.2	18.5	12.1	11.1	32.3
BTA 0.1M/EtOH, re-used	0.0059	0.0063	0.0075	0.0072	0.0079	24.8	23.9	13.0	22.1	32.3

Inhibitive Efficiency calculated using: 0.0079(24h), 0.0083(48h), 0.0086(168h), 0.0092(504h), 0.0096(840h).

Fractional Factorial Fit

```
Estimated Effects and Coefficients for 24 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant               0.005767    0.000161   35.88  0.000
A         -0.001133 -0.000567    0.000161   -3.53  0.008
B         -0.003067 -0.001533    0.000161   -9.54  0.000
A*B        0.000800  0.000400    0.000161    2.49  0.038

Analysis of Variance for 24 (coded units)

Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00003207  0.00003207  0.00001603  51.72  0.000
2-Way Interactions    1  0.00000192  0.00000192  0.00000192   6.19  0.038
Residual Error        8  0.00000248  0.00000248  0.00000031
  Pure Error          8  0.00000248  0.00000248  0.00000031
Total                11  0.00003647

Unusual Observations for 24

Obs         24        Fit  StDev Fit   Residual   St Resid
 10   0.005500   0.004400   0.000321   0.001100       2.42R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant               0.006117    0.000140   43.63  0.000
A         -0.001067 -0.000533    0.000140   -3.80  0.005
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B         -0.002967 -0.001483    0.000140  -10.58  0.000
A*B        0.000733  0.000367    0.000140    2.62  0.031

Analysis of Variance for 48 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           2  0.00002982  0.00002982  0.00001491  63.22  0.000
2-Way Interactions     1  0.00000161  0.00000161  0.00000161   6.84  0.031
Residual Error         8  0.00000189  0.00000189  0.00000024
  Pure Error           8  0.00000189  0.00000189  0.00000024
Total                 11  0.00003332

Unusual Observations for 48

Obs         48        Fit  StDev Fit   Residual   St Resid
 10   0.005700   0.004800   0.000280   0.000900       2.27R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant              0.006967    0.000162   43.11  0.000
A         -0.000533 -0.000267    0.000162   -1.65  0.137
B         -0.002833 -0.001417    0.000162   -8.77  0.000
A*B        0.000767  0.000383    0.000162    2.37  0.045

Analysis of Variance for 168 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           2  0.00002494  0.00002494  0.00001247  39.79  0.000
2-Way Interactions     1  0.00000176  0.00000176  0.00000176   5.63  0.045
Residual Error         8  0.00000251  0.00000251  0.00000031
  Pure Error           8  0.00000251  0.00000251  0.00000031
Total                 11  0.00002921

Estimated Effects and Coefficients for 504 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant              0.007367    0.000151   48.89  0.000
A         -0.000233 -0.000117    0.000151   -0.77  0.461
B         -0.002300 -0.001150    0.000151   -7.63  0.000
A*B        0.000667  0.000333    0.000151    2.21  0.058

Analysis of Variance for 504 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           2  0.00001603  0.00001603  0.00000802  29.42  0.000
2-Way Interactions     1  0.00000133  0.00000133  0.00000133   4.89  0.058
Residual Error         8  0.00000218  0.00000218  0.00000027
  Pure Error           8  0.00000218  0.00000218  0.00000027
Total                 11  0.00001955

Unusual Observations for 504

Obs        504        Fit  StDev Fit   Residual   St Resid
  6   0.007200   0.008067   0.000301  -0.000867      -2.03R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term         Effect      Coef  StDev Coef       T      P
```
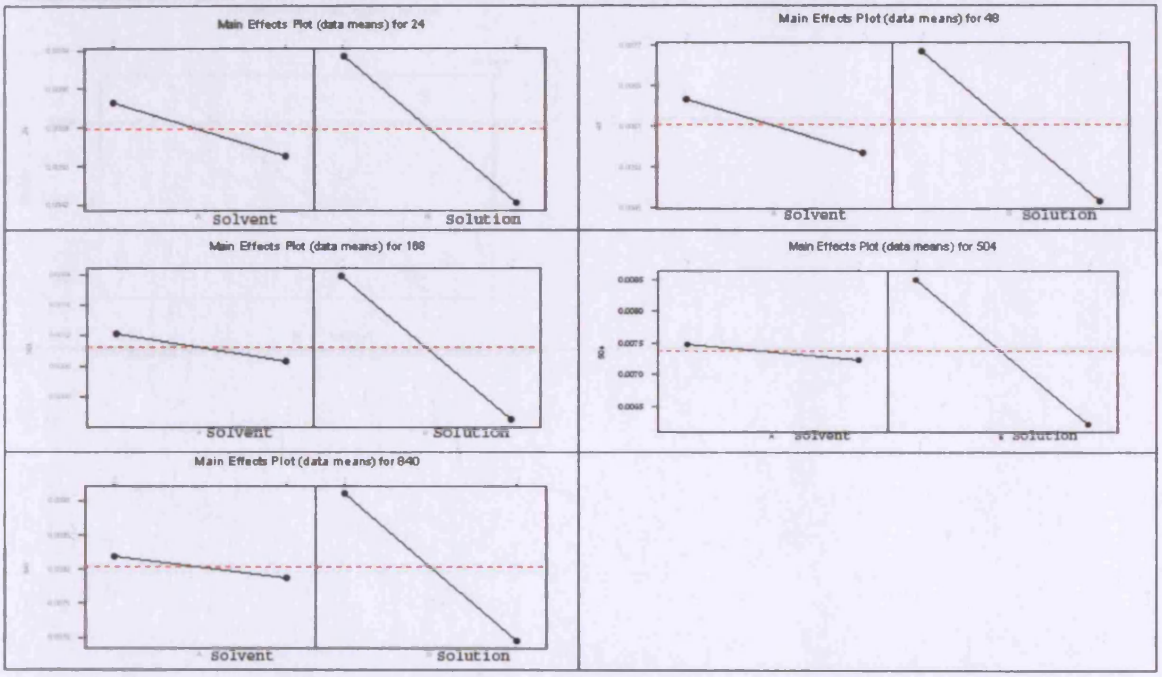
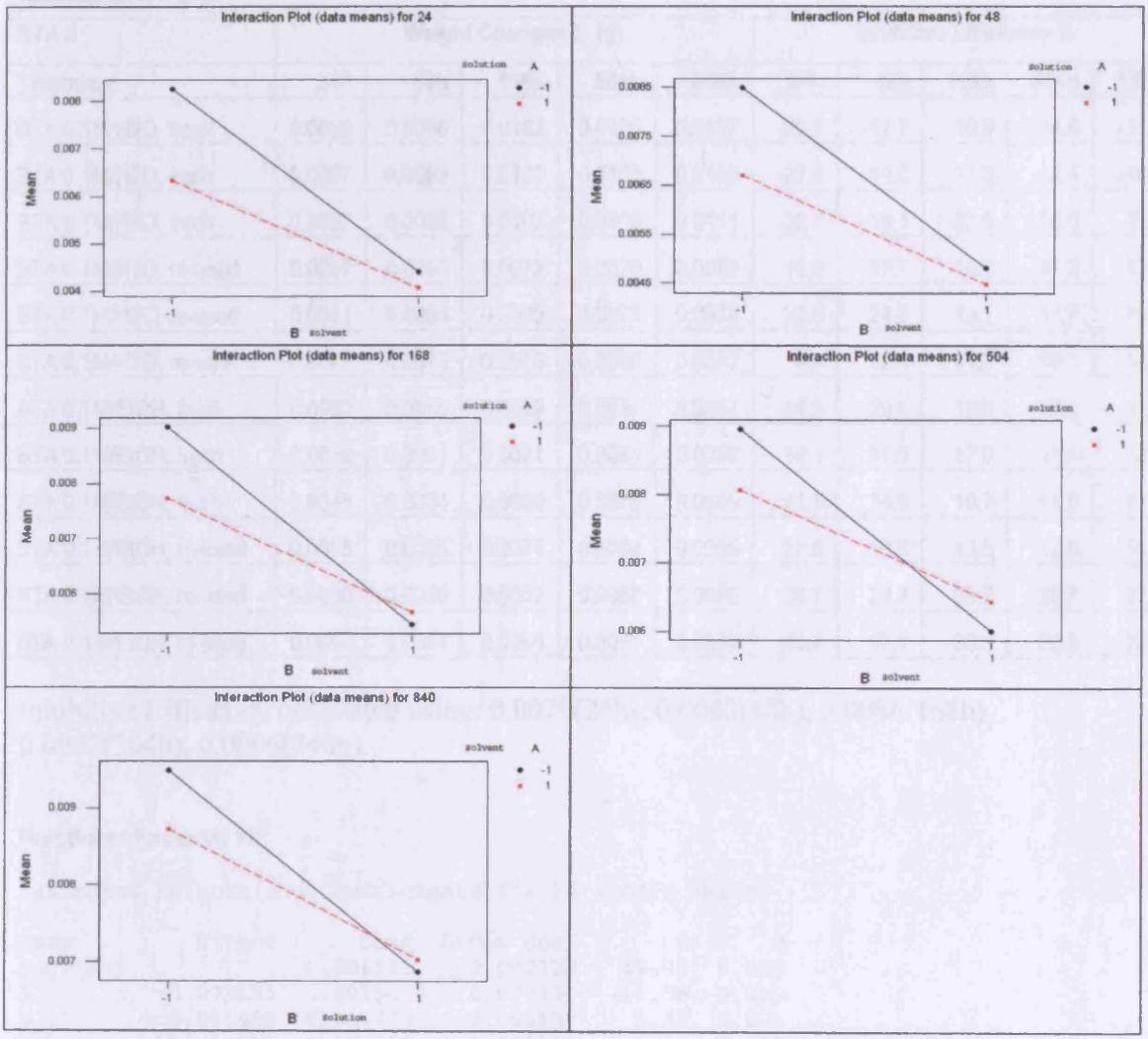

```
Constant              0.008033    0.000141   57.10  0.000
A          -0.000300 -0.000150    0.000141   -1.07  0.317
B          -0.002167 -0.001083    0.000141   -7.70  0.000
A*B         0.000467  0.000233    0.000141    1.66  0.136

Analysis of Variance for 840 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS       F      P
Main Effects           2  0.00001435  0.00001435  0.00000718   30.22  0.000
2-Way Interactions     1  0.00000065  0.00000065  0.00000065    2.75  0.136
Residual Error         8  0.00000190  0.00000190  0.00000024
  Pure Error           8  0.00000190  0.00000190  0.00000024
Total                 11  0.00001691

Unusual Observations for 840

Obs        840         Fit  StDev Fit    Residual   St Resid
  6   0.007900   0.008733   0.000281   -0.000833      -2.09R

R denotes an observation with a large standardized residual

Alias Structure

I
A
B
A*B
```

Main Effect Plots



Interaction Plots



BTA 8	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.1M/H2O, fresh	0.0096	0.0098	0.0102	0.0105	0.0107	-22.1	-17.7	-18.9	-14.0	-11.2
BTA 0.1M/H2O, fresh	0.0097	0.0099	0.0101	0.0103	0.0106	-22.4	-19.0	-17.3	-12.4	-10.1
BTA 0.1M/H2O, fresh	0.0097	0.0098	0.0106	0.0109	0.0111	-22.7	-18.1	-23.6	-18.5	-15.9
BTA 0.1M/H2O, re-used	0.0067	0.0068	0.0072	0.0076	0.0080	15.0	17.7	16.0	17.2	17.1
BTA 0.1M/H2O, re-used	0.0061	0.0063	0.0070	0.0075	0.0078	23.0	24.3	19.1	18.7	18.4
BTA 0.1M/H2O, re-used	0.0071	0.0073	0.0076	0.0080	0.0082	9.7	12.4	11.7	13.3	14.6
BTA 0.1M/EtOH, fresh	0.0052	0.0058	0.0069	0.0077	0.0084	34.5	29.6	19.9	16.0	12.9
BTA 0.1M/EtOH, fresh	0.0052	0.0061	0.0071	0.0081	0.0088	34.1	27.0	17.0	11.8	8.7
BTA 0.1M/EtOH, fresh	0.0045	0.0054	0.0069	0.0078	0.0085	43.5	34.9	19.7	14.8	11.1
BTA 0.1M/EtOH, re-used	0.0058	0.0058	0.0074	0.0080	0.0085	27.0	30.5	13.5	12.6	11.1
BTA 0.1M/EtOH, re-used	0.0050	0.0050	0.0057	0.0068	0.0070	36.7	39.7	33.7	25.7	27.0
BTA 0.1M/EtOH, re-used	0.0044	0.0044	0.0060	0.0071	0.0072	44.4	47.1	30.3	23.3	24.5

Inhibitive Efficiency calculated using: 0.0079(24h), 0.0083(48h), 0.0086(168h), 0.0092(504h), 0.0096(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006583	0.000138	47.73	0.000
A	-0.003133	-0.001567	0.000138	-11.36	0.000
B	0.001467	0.000733	0.000138	5.32	0.001
A*B	-0.001567	-0.000783	0.000138	-5.68	0.000

Analysis of Variance for 24 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00003591	0.00003591	0.00001795	78.63	0.000
2-Way Interactions	1	0.00000736	0.00000736	0.00000736	32.25	0.000
Residual Error	8	0.00000183	0.00000183	0.00000023		
Pure Error	8	0.00000183	0.00000183	0.00000023		
Total	11	0.00004510				

Estimated Effects and Coefficients for 48 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006867	0.000135	51.00	0.000
A	-0.002900	-0.001450	0.000135	-10.77	0.000
B	0.001867	0.000933	0.000135	6.93	0.000
A*B	-0.001167	-0.000583	0.000135	-4.33	0.003

Analysis of Variance for 48 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00003568	0.00003568	0.00001784	82.03	0.000
2-Way Interactions	1	0.00000408	0.00000408	0.00000408	18.77	0.003
Residual Error	8	0.00000174	0.00000174	0.00000022		
Pure Error	8	0.00000174	0.00000174	0.00000022		
Total	11	0.00004151				

Estimated Effects and Coefficients for 168 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007725	0.000144	53.52	0.000
A	-0.002117	-0.001058	0.000144	-7.33	0.000
B	0.001817	0.000908	0.000144	6.29	0.000
A*B	-0.001217	-0.000608	0.000144	-4.21	0.003

Analysis of Variance for 168 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00002334	0.00002334	0.00001167	46.68	0.000
2-Way Interactions	1	0.00000444	0.00000444	0.00000444	17.76	0.003
Residual Error	8	0.00000200	0.00000200	0.00000025		
Pure Error	8	0.00000200	0.00000200	0.00000025		
Total	11	0.00002978				

Unusual Observations for 168

Obs	168	Fit	StDev Fit	Residual	St Resid
1	0.007400	0.006367	0.000289	0.001033	2.53R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008358	0.000111	74.97	0.000
A	-0.001550	-0.000775	0.000111	-6.95	0.000
B	0.001717	0.000858	0.000111	7.70	0.000
A*B	-0.001150	-0.000575	0.000111	-5.16	0.001

Analysis of Variance for 504 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001605	0.00001605	0.00000802	53.79	0.000
2-Way Interactions	1	0.00000397	0.00000397	0.00000397	26.60	0.001
Residual Error	8	0.00000119	0.00000119	0.00000015		
Pure Error	8	0.00000119	0.00000119	0.00000015		
Total	11	0.00002121				

Unusual Observations for 504

Obs	504	Fit	StDev Fit	Residual	St Resid
1	0.008000	0.007300	0.000223	0.000700	2.22R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008733	0.000130	66.95	0.000
A	-0.001333	-0.000667	0.000130	-5.11	0.001
B	0.001900	0.000950	0.000130	7.28	0.000
A*B	-0.000900	-0.000450	0.000130	-3.45	0.009

Analysis of Variance for 840 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001616	0.00001616	0.00000808	39.58	0.000
2-Way Interactions	1	0.00000243	0.00000243	0.00000243	11.90	0.009
Residual Error	8	0.00000163	0.00000163	0.00000020		
Pure Error	8	0.00000163	0.00000163	0.00000020		
Total	11	0.00002023				

Unusual Observations for 840

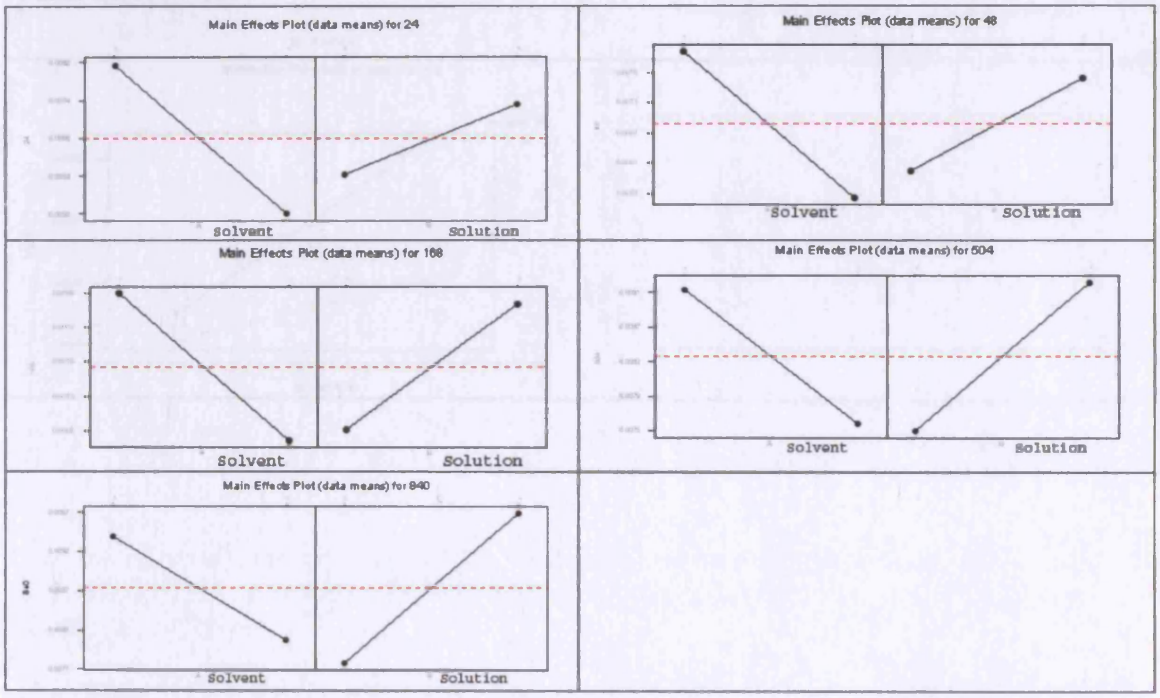
Obs	840	Fit	StDev Fit	Residual	St Resid
1	0.008500	0.007567	0.000261	0.000933	2.53R

R denotes an observation with a large standardized residual

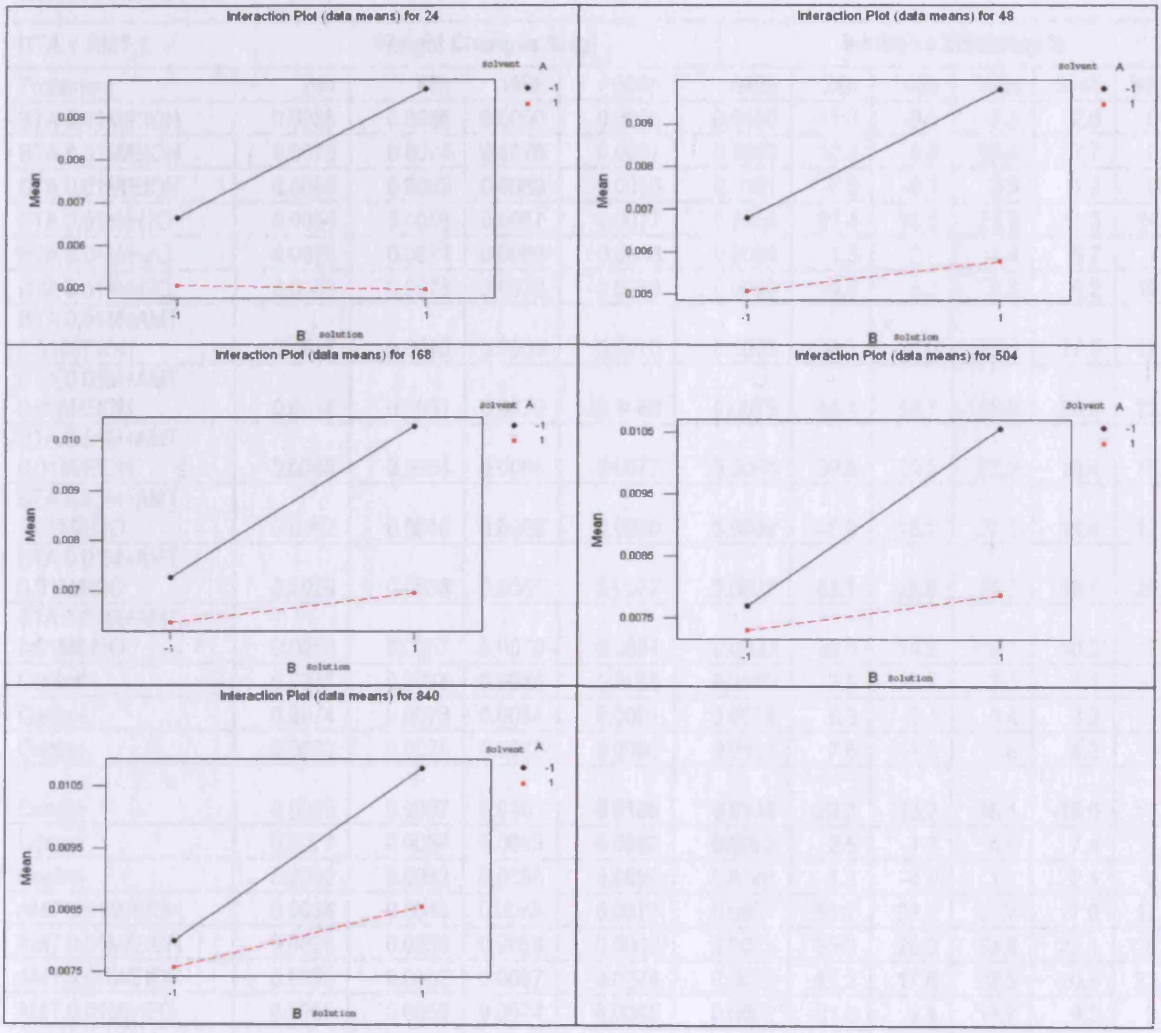
Alias Structure

I
A
B
A*B

Main Effect Plots



Interaction Plots



BTA + AMT 1	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.01M/EtOH	0.0088	0.0088	0.0090	0.0096	0.0100	-11.0	-9.6	-3.3	-2.6	0.8
BTA 0.01M/EtOH	0.0070	0.0074	0.0078	0.0087	0.0093	10.9	4.9	10.4	7.7	8.2
BTA 0.01M/EtOH	0.0085	0.0085	0.0089	0.0095	0.0101	-7.9	-9.1	-2.9	-1.2	0.1
BTA 0.01M/H2O	0.0054	0.0056	0.0067	0.0077	0.0086	31.4	18.6	23.3	18.3	14.9
BTA 0.01M/H2O	0.0078	0.0074	0.0080	0.0088	0.0094	1.3	2.9	8.4	6.7	7.2
BTA 0.01M/H2O	0.0083	0.0073	0.0078	0.0088	0.0090	-4.9	4.3	9.8	6.2	10.5
BTA 0.01M+AMT 0.01M/EtOH	0.0036	0.0040	0.0059	0.0078	0.0083	54.3	28.0	32.2	17.5	17.8
BTA 0.01M+AMT 0.01M/EtOH	0.0044	0.0051	0.0070	0.0069	0.0079	44.1	14.7	19.6	26.8	22.0
BTA 0.01M+AMT 0.01M/EtOH	0.0048	0.0054	0.0066	0.0077	0.0085	39.6	19.3	23.9	18.4	15.5
BTA 0.01M+AMT 0.01M/H2O	0.0042	0.0046	0.0069	0.0080	0.0089	46.9	16.2	21.0	14.4	12.0
BTA 0.01M+AMT 0.01M/H2O	0.0029	0.0036	0.0061	0.0077	0.0072	63.1	25.5	29.7	18.1	28.5
BTA 0.01M+AMT 0.01M/H2O	0.0050	0.0057	0.0070	0.0084	0.0093	36.9	14.2	19.1	10.9	7.8
Control	0.0076	0.0078	0.0085	0.0095	0.0103	3.8	-3.7	2.3	-1.1	-2.0
Control	0.0074	0.0078	0.0084	0.0091	0.0098	6.3	-2.4	3.4	3.2	3.0
Control	0.0073	0.0075	0.0083	0.0090	0.0101	7.6	-1.2	4.6	4.3	0.0
Control	0.0095	0.0097	0.0101	0.0109	0.0113	-20.3	-23.2	-16.1	-16.0	-11.9
Control	0.0077	0.0080	0.0083	0.0087	0.0093	2.5	-1.2	4.6	7.4	7.9
Control	0.0080	0.0083	0.0086	0.0092	0.0101	-1.3	-4.9	1.1	2.1	0.5
AMT 0.01M/EtOH	0.0034	0.0046	0.0065	0.0078	0.0084	56.7	21.2	25.7	17.0	17.1
AMT 0.01M/EtOH	0.0035	0.0039	0.0058	0.0069	0.0075	55.3	29.3	33.4	27.1	25.6
AMT 0.01M/EtOH	0.0039	0.0052	0.0067	0.0074	0.0079	51.2	17.8	22.5	20.8	22.0
AMT 0.01M/H2O	0.0055	0.0059	0.0074	0.0085	0.0092	31.0	9.5	14.7	9.3	9.1
AMT 0.01M/H2O	0.0066	0.0068	0.0085	0.0095	0.0100	16.9	-3.5	2.4	-0.9	1.2
AMT 0.01M/H2O	0.0065	0.0068	0.0080	0.0092	0.0096	17.7	2.2	7.9	2.6	5.4

The inhibitive efficiency was calculated using the average weight change of the control coupons of the experiment: 0.0079 (24h), 0.0082 (48h), 0.0087 (168h), 0.0094 (504h) and 0.0101 (840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006246	0.000181	34.43	0.000
BTA	-0.000708	-0.000354	0.000181	-1.95	0.069
AMT	-0.003058	-0.001529	0.000181	-8.43	0.000
Solvent	-0.000408	-0.000204	0.000181	-1.13	0.277

BTA*AMT	-0.000425	-0.000212	0.000181	-1.17	0.259
BTA*Solvent	0.000992	0.000496	0.000181	2.73	0.015
AMT*Solvent	-0.000392	-0.000196	0.000181	-1.08	0.296
BTA*AMT*Solvent	0.000042	0.000021	0.000181	0.11	0.910

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00006013	0.00006013	0.00002004	25.39	0.000
2-Way Interactions	3	0.00000790	0.00000790	0.00000263	3.34	0.046
3-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.01	0.910
Residual Error	16	0.00001263	0.00001263	0.00000079		
Pure Error	16	0.00001263	0.00001263	0.00000079		
Total	23	0.00008068				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
6	0.005400	0.007167	0.000513	-0.001767	-2.44R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006533	0.000153	42.77	0.000
BTA	-0.000833	-0.000417	0.000153	-2.73	0.015
AMT	-0.002617	-0.001308	0.000153	-8.57	0.000
Solvent	-0.000217	-0.000108	0.000153	-0.71	0.488
BTA*AMT	-0.000150	-0.000075	0.000153	-0.49	0.630
BTA*Solvent	0.001050	0.000525	0.000153	3.44	0.003
AMT*Solvent	-0.000467	-0.000233	0.000153	-1.53	0.146
BTA*AMT*Solvent	-0.000167	-0.000083	0.000153	-0.55	0.593

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00004553	0.00004553	0.00001518	27.10	0.000
2-Way Interactions	3	0.00000806	0.00000806	0.00000269	4.80	0.014
3-Way Interactions	1	0.00000017	0.00000017	0.00000017	0.30	0.593
Residual Error	16	0.00000896	0.00000896	0.00000056		
Pure Error	16	0.00000896	0.00000896	0.00000056		
Total	23	0.00006271				

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007621	0.000123	61.97	0.000
BTA	-0.000625	-0.000313	0.000123	-2.54	0.022
AMT	-0.001492	-0.000746	0.000123	-6.07	0.000
Solvent	-0.000325	-0.000162	0.000123	-1.32	0.205
BTA*AMT	0.000042	0.000021	0.000123	0.17	0.868
BTA*Solvent	0.000775	0.000387	0.000123	3.15	0.006
AMT*Solvent	-0.000558	-0.000279	0.000123	-2.27	0.037
BTA*AMT*Solvent	-0.000058	-0.000029	0.000123	-0.24	0.816

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001633	0.00001633	0.00000544	15.00	0.000
2-Way Interactions	3	0.00000548	0.00000548	0.00000183	5.04	0.012
3-Way Interactions	1	0.00000002	0.00000002	0.00000002	0.06	0.816
Residual Error	16	0.00000581	0.00000581	0.00000036		

Pure Error	16	0.00000581	0.00000581	0.00000036
Total	23	0.00002764		

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
1	0.010100	0.009000	0.000348	0.001100	2.24R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008563	0.000122	70.40	0.000
BTA	-0.000525	-0.000263	0.000122	-2.16	0.046
AMT	-0.001125	-0.000562	0.000122	-4.63	0.000
Solvent	-0.000442	-0.000221	0.000122	-1.82	0.088
BTA*AMT	0.000025	0.000012	0.000122	0.10	0.919
BTA*Solvent	0.000575	0.000288	0.000122	2.36	0.031
AMT*Solvent	-0.000658	-0.000329	0.000122	-2.71	0.016
BTA*AMT*Solvent	-0.000042	-0.000021	0.000122	-0.17	0.866

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001042	0.00001042	0.00000347	9.78	0.001
2-Way Interactions	3	0.00000459	0.00000459	0.00000153	4.31	0.021
3-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.03	0.866
Residual Error	16	0.00000568	0.00000568	0.00000036		
Pure Error	16	0.00000568	0.00000568	0.00000036		
Total	23	0.00002070				

Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid
1	0.010900	0.009600	0.000344	0.001300	2.67R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.009183	0.000125	73.26	0.000
BTA	-0.000617	-0.000308	0.000125	-2.46	0.026
AMT	-0.001183	-0.000592	0.000125	-4.72	0.000
Solvent	-0.000283	-0.000142	0.000125	-1.13	0.275
BTA*AMT	0.000133	0.000067	0.000125	0.53	0.602
BTA*Solvent	0.000567	0.000283	0.000125	2.26	0.038
AMT*Solvent	-0.000600	-0.000300	0.000125	-2.39	0.029
BTA*AMT*Solvent	0.000083	0.000042	0.000125	0.33	0.744

Analysis of Variance for 840h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001116	0.00001116	0.00000372	9.87	0.001
2-Way Interactions	3	0.00000419	0.00000419	0.00000140	3.71	0.034
3-Way Interactions	1	0.00000004	0.00000004	0.00000004	0.11	0.744
Residual Error	16	0.00000603	0.00000603	0.00000038		
Pure Error	16	0.00000603	0.00000603	0.00000038		
Total	23	0.00002143				

Unusual Observations for 840h

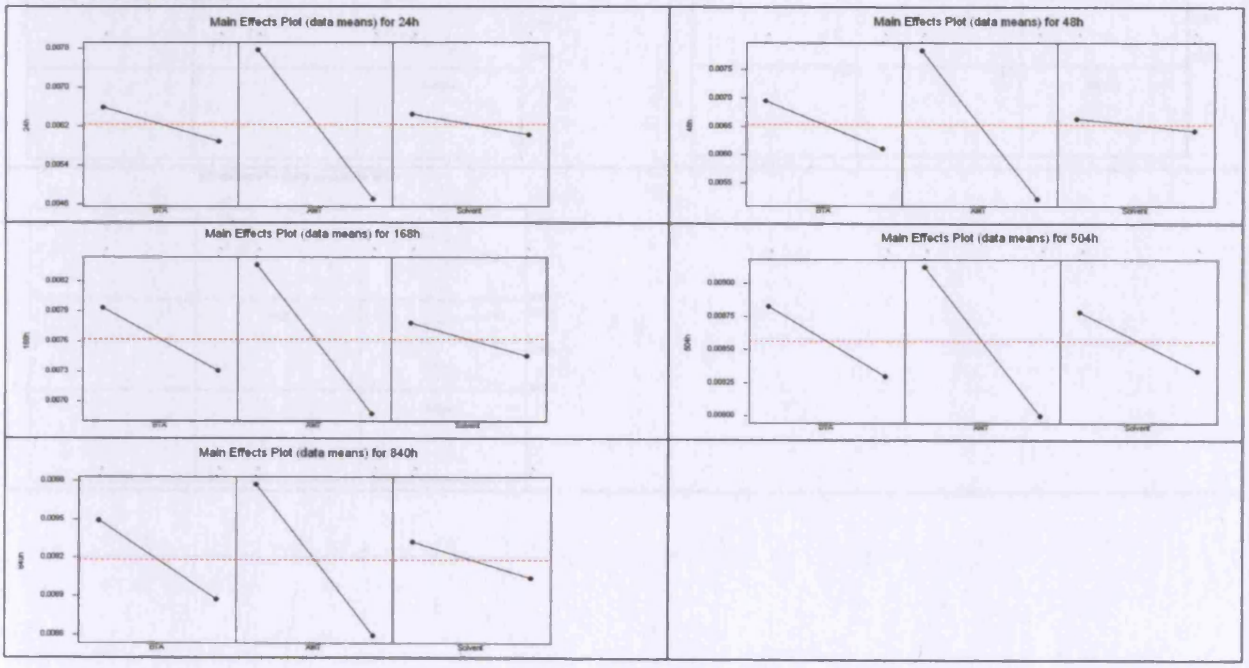
Obs	840h	Fit	StDev Fit	Residual	St Resid
1	0.011300	0.010233	0.000355	0.001067	2.13R
7	0.007200	0.008467	0.000355	-0.001267	-2.53R

R denotes an observation with a large standardized residual

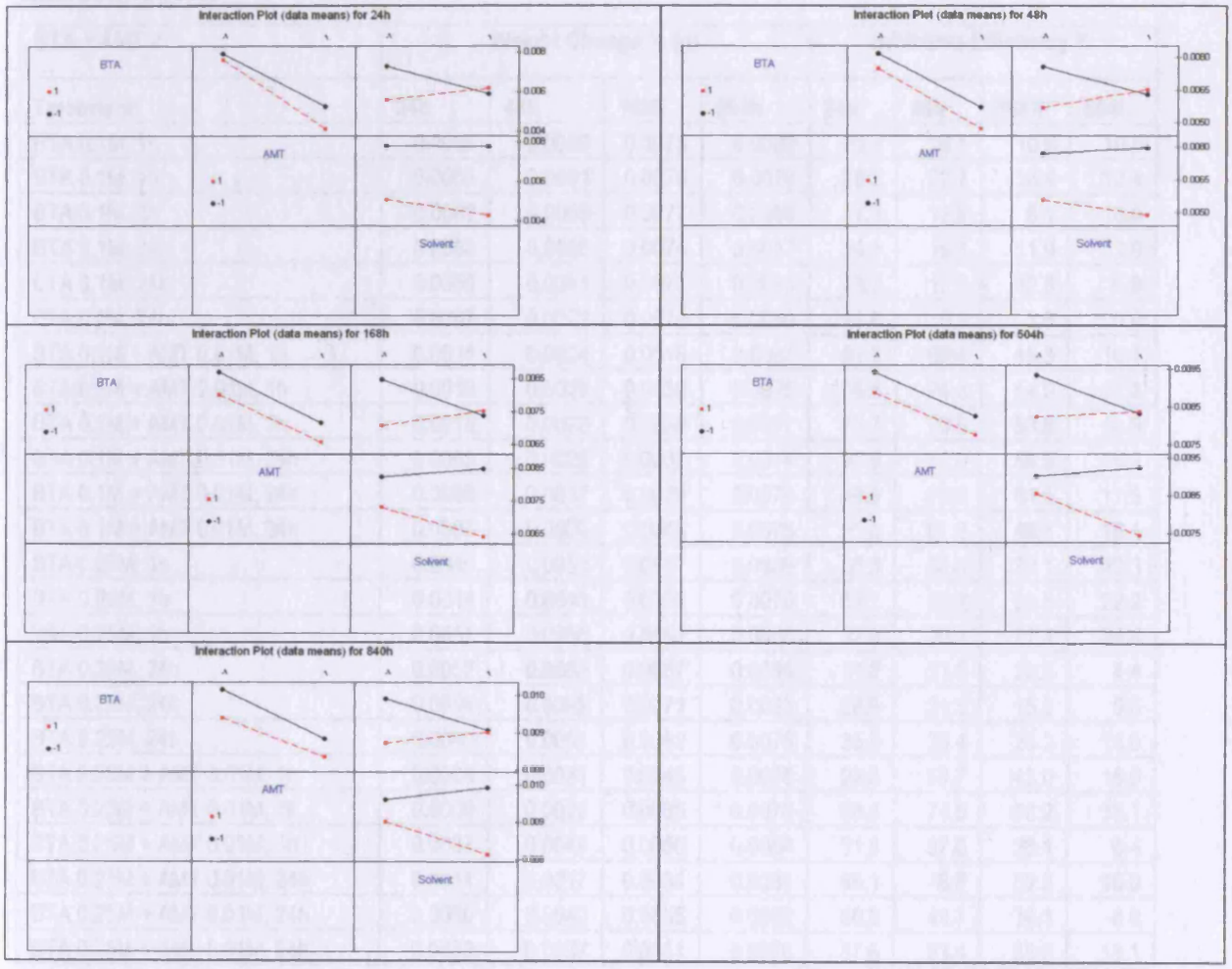
Alias Structure

I
BTA
AMT
Solvent
BTA*AMT
BTA*Solvent
AMT*Solvent
BTA*AMT*Solvent

BTA and AMT 3f
Main Effect Plots



Interaction Plots



BTA + AMT 2	Weight Change % (g)				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M, 1h	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M, 1h	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M, 1h	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M, 24h	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M, 24h	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M, 24h	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M + AMT 0.01M, 1h	0.0014	0.0024	0.0046	0.0081	81.8	69.4	45.3	10.1
BTA 0.1M + AMT 0.01M, 1h	0.0010	0.0020	0.0039	0.0075	86.4	74.3	54.0	16.3
BTA 0.1M + AMT 0.01M, 1h	0.0016	0.0023	0.0039	0.0077	78.7	70.5	53.6	14.9
BTA 0.1M + AMT 0.01M, 24h	0.0005	0.0022	0.0037	0.0074	92.9	71.6	56.5	18.2
BTA 0.1M + AMT 0.01M, 24h	0.0009	0.0017	0.0030	0.0074	88.6	79.0	64.6	17.5
BTA 0.1M + AMT 0.01M, 24h	0.0007	0.0030	0.0045	0.0076	91.0	61.8	46.6	16.1
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.0070	42.1	39.2	34.5	22.2
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M + AMT 0.01M, 1h	0.0006	0.0031	0.0048	0.0076	92.0	60.7	43.0	15.9
BTA 0.25M + AMT 0.01M, 1h	0.0009	0.0020	0.0035	0.0078	88.4	74.5	58.2	13.1
BTA 0.25M + AMT 0.01M, 1h	0.0037	0.0049	0.0060	0.0084	51.3	37.6	28.1	6.4
BTA 0.25M + AMT 0.01M, 24h	0.0011	0.0017	0.0034	0.0081	86.1	78.6	59.3	10.0
BTA 0.25M + AMT 0.01M, 24h	0.0030	0.0040	0.0055	0.0082	60.9	49.7	34.1	8.8
BTA 0.25M + AMT 0.01M, 24h	0.0032	0.0037	0.0051	0.0078	57.6	53.4	38.9	13.1

The Inhibitive efficiency was calculated using: 0.0076(24h), 0.0079(48h), 0.0084(168h) and 0.0090 (504h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.003504	0.000161	21.70	0.000
BTA	0.000058	0.000029	0.000161	0.18	0.859
AMT	-0.003908	-0.001954	0.000161	-12.10	0.000
Immersio	0.000192	0.000096	0.000161	0.59	0.561
BTA*AMT	0.001008	0.000504	0.000161	3.12	0.007
BTA*Immersio	0.000342	0.000171	0.000161	1.06	0.306
AMT*Immersio	-0.000158	-0.000079	0.000161	-0.49	0.631
BTA*AMT*Immersio	0.000325	0.000163	0.000161	1.01	0.329

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00009189	0.00009189	0.00003063	48.94	0.000

2-Way Interactions	3	0.00000695	0.00000695	0.00000232	3.70	0.034
3-Way Interactions	1	0.00000063	0.00000063	0.00000063	1.01	0.329
Residual Error	16	0.00001001	0.00001001	0.00000063		
Pure Error	16	0.00001001	0.00001001	0.00000063		
Total	23	0.00010949				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
13	0.001100	0.002433	0.000457	-0.001333	-2.06R
23	0.003700	0.001733	0.000457	0.001967	3.04R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.004383	0.000163	26.91	0.000
BTA	-0.000050	-0.000025	0.000163	-0.15	0.880
AMT	-0.003267	-0.001633	0.000163	-10.03	0.000
Immersio	0.000250	0.000125	0.000163	0.77	0.454
BTA*AMT	0.001017	0.000508	0.000163	3.12	0.007
BTA*Immersio	0.000000	0.000000	0.000163	0.00	1.000
AMT*Immersio	-0.000317	-0.000158	0.000163	-0.97	0.345
BTA*AMT*Immersio	-0.000133	-0.000067	0.000163	-0.41	0.688

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00006442	0.00006442	0.00002147	33.73	0.000
2-Way Interactions	3	0.00000680	0.00000680	0.00000227	3.56	0.038
3-Way Interactions	1	0.00000011	0.00000011	0.00000011	0.17	0.688
Residual Error	16	0.00001019	0.00001019	0.00000064		
Pure Error	16	0.00001019	0.00001019	0.00000064		
Total	23	0.00008151				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
11	0.002000	0.003333	0.000461	-0.001333	-2.05R
13	0.001700	0.003133	0.000461	-0.001433	-2.20R
23	0.004900	0.003333	0.000461	0.001567	2.40R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.005583	0.000145	38.38	0.000
BTA	-0.000233	-0.000117	0.000145	-0.80	0.434
AMT	-0.002517	-0.001258	0.000145	-8.65	0.000
Immersio	0.000133	0.000067	0.000145	0.46	0.653
BTA*AMT	0.001017	0.000508	0.000145	3.49	0.003
BTA*Immersio	0.000267	0.000133	0.000145	0.92	0.373
AMT*Immersio	-0.000383	-0.000192	0.000145	-1.32	0.206
BTA*AMT*Immersio	-0.000117	-0.000058	0.000145	-0.40	0.694

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003844	0.00003844	0.00001281	25.22	0.000
2-Way Interactions	3	0.00000751	0.00000751	0.00000250	4.93	0.013
3-Way Interactions	1	0.00000008	0.00000008	0.00000008	0.16	0.694

Residual Error	16	0.00000813	0.00000813	0.00000051
Pure Error	16	0.00000813	0.00000813	0.00000051
Total	23	0.00005415		

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
11	0.003500	0.004767	0.000411	-0.001267	-2.18R
13	0.003400	0.004667	0.000411	-0.001267	-2.18R
23	0.006000	0.004767	0.000411	0.001233	2.12R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007879	0.000061	130.18	0.000
BTA	-0.000208	-0.000104	0.000061	-1.72	0.105
AMT	-0.000158	-0.000079	0.000061	-1.31	0.209
Immersio	0.000475	0.000238	0.000061	3.92	0.001
BTA*AMT	0.000575	0.000288	0.000061	4.75	0.000
BTA*Immersio	0.000242	0.000121	0.000061	2.00	0.063
AMT*Immersio	-0.000575	-0.000287	0.000061	-4.75	0.000
BTA*AMT*Immersio	-0.000042	-0.000021	0.000061	-0.34	0.735

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00000176	0.00000176	0.00000059	6.69	0.004
2-Way Interactions	3	0.00000432	0.00000432	0.00000144	16.37	0.000
3-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.12	0.735
Residual Error	16	0.00000141	0.00000141	0.00000009		
Pure Error	16	0.00000141	0.00000141	0.00000009		
Total	23	0.00000750				

Unusual Observations for 504h

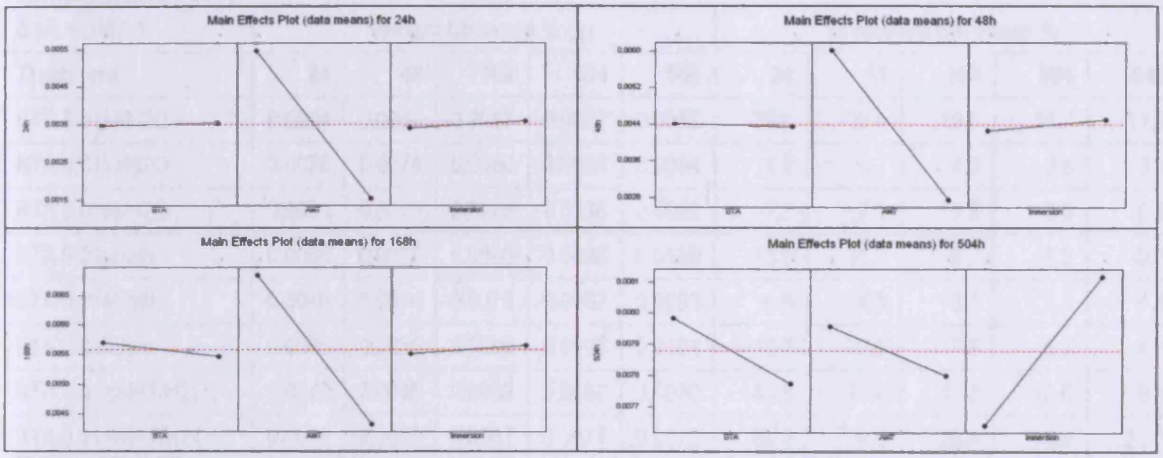
Obs	504h	Fit	StDev Fit	Residual	St Resid
18	0.007600	0.008233	0.000171	-0.000633	-2.62R

R denotes an observation with a large standardized residual

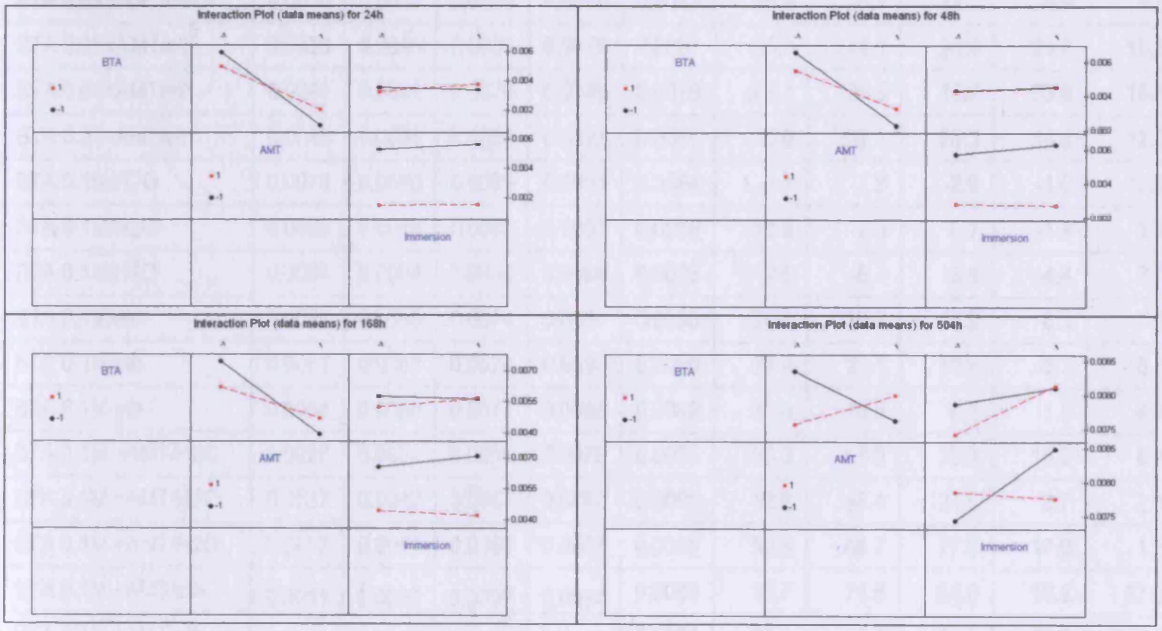
Alias Structure

I
BTA
AMT
Immersion
BTA*AMT
BTA*Immersion
AMT*Immersion
BTA*AMT*Immersion

Main Effect Plots



Interaction Plots



BTA + AMT 3	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24	48	168	504	840	24	48	168	504	840
BTA 0.01M/H2O	0.0054	0.0056	0.0067	0.0077	0.0086	29.6	29.4	19.6	14.7	11.4
BTA 0.01M/H2O	0.0078	0.0074	0.0080	0.0088	0.0094	-1.2	6.7	4.0	2.6	3.4
BTA 0.01M/H2O	0.0083	0.0073	0.0078	0.0088	0.0090	-7.7	7.1	5.5	2.0	6.8
BTA 0.01M/eth	0.0088	0.0088	0.0090	0.0096	0.0100	-13.9	-11.3	-8.2	-7.2	-3.3
BTA 0.01M/eth	0.0070	0.0074	0.0078	0.0087	0.0093	8.6	6.9	6.1	3.6	4.4
BTA 0.01M/eth	0.0085	0.0085	0.0089	0.0095	0.0101	-10.7	-7.6	-7.8	-5.7	-4.0
BTA 0.01+AMT/H2O	0.0042	0.0046	0.0069	0.0080	0.0089	45.5	41.6	17.2	10.6	8.4
BTA 0.01+AMT/H2O	0.0029	0.0036	0.0061	0.0077	0.0072	62.2	54.9	26.4	14.4	25.5
BTA 0.01+AMT/H2O	0.0050	0.0057	0.0070	0.0084	0.0093	35.3	28.1	15.2	6.9	4.0
BTA 0.01+AMT/eth	0.0036	0.0040	0.0059	0.0078	0.0087	53.1	49.1	28.9	13.8	10.0
BTA 0.01+AMT/eth	0.0044	0.0051	0.0070	0.0069	0.0079	42.7	35.5	15.7	23.6	18.8
BTA 0.01+AMT/eth	0.0048	0.0054	0.0066	0.0077	0.0085	38.0	32.1	20.3	14.8	12.0
BTA 0.1M/H2O	0.0079	0.0080	0.0085	0.0091	0.0094	-3.0	-1.3	-2.9	-1.0	3.5
BTA 0.1M/H2O	0.0085	0.0085	0.0082	0.0091	0.0096	-10.9	-7.5	0.7	-1.4	1.3
BTA 0.1M/H2O	0.0084	0.0084	0.0088	0.0094	0.0095	-9.6	-6.7	-5.8	-4.4	2.1
BTA 0.1M/eth	0.0062	0.0065	0.0074	0.0084	0.0090	20.1	17.7	11.3	6.3	7.1
BTA 0.1M/eth	0.0061	0.0063	0.0074	0.0090	0.0090	21.4	20.1	10.7	-0.3	6.7
BTA 0.1M/eth	0.0064	0.0066	0.0077	0.0088	0.0092	17.0	15.9	6.7	1.9	4.7
BTA 0.1M +AMT/H2O	0.0026	0.0032	0.0050	0.0076	0.0091	66.3	58.9	39.8	15.2	6.7
BTA 0.1M +AMT/H2O	0.0037	0.0042	0.0063	0.0082	0.0095	52.6	46.4	24.5	8.7	2.5
BTA 0.1M +AMT/H2O	0.0037	0.0041	0.0060	0.0081	0.0095	52.6	48.7	27.6	10.0	1.8
BTA 0.1M +AMT/eth	0.0011	0.0022	0.0037	0.0074	0.0080	85.7	71.6	56.0	18.2	17.5
BTA 0.1M +AMT/eth	0.0010	0.0017	0.0027	0.0073	0.0081	86.6	79.0	66.9	19.0	16.5
BTA 0.1M +AMT/eth	0.0009	0.0020	0.0035	0.0076	0.0086	88.8	74.5	58.0	16.1	11.7

The inhibitive efficiency was calculated using: 0.0077 (24h), 0.0079(48h), 0.0083(168h), 0.0090(504h), 0.0097(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.005300	0.000167	31.69	0.000
BTA	-0.001183	-0.000592	0.000167	-3.54	0.003
AMT	-0.004283	-0.002142	0.000167	-12.81	0.000
Solvent	-0.000800	-0.000400	0.000167	-2.39	0.029
BTA*AMT	-0.000800	-0.000400	0.000167	-2.39	0.029
BTA*Solvent	-0.001383	-0.000692	0.000167	-4.14	0.001

```
AMT*Solvent       -0.000250 -0.000125    0.000167   -0.75  0.466
BTA*AMT*Solvent    0.000100  0.000050    0.000167    0.30  0.769

Analysis of Variance for 24 (coded units)

Source               DF      Seq SS     Adj SS     Adj MS      F      P
Main Effects          3  0.00012232 0.00012232 0.00004077  60.74  0.000
2-Way Interactions    3  0.00001570 0.00001570 0.00000523   7.79  0.002
3-Way Interactions    1  0.00000006 0.00000006 0.00000006   0.09  0.769
Residual Error       16  0.00001074 0.00001074 0.00000067
  Pure Error         16  0.00001074 0.00001074 0.00000067
Total                23  0.00014882

Unusual Observations for 24

Obs         24        Fit  StDev Fit   Residual   St Resid
  4   0.005400   0.007167   0.000473  -0.001767      -2.64R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48 (coded units)

Term                Effect      Coef  StDev Coef       T      P
Constant                     0.005629    0.000138   40.70  0.000
BTA               -0.000975 -0.000488    0.000138   -3.52  0.003
AMT               -0.003625 -0.001812    0.000138  -13.10  0.000
Solvent           -0.000508 -0.000254    0.000138   -1.84  0.085
BTA*AMT           -0.000858 -0.000429    0.000138   -3.10  0.007
BTA*Solvent       -0.001342 -0.000671    0.000138   -4.85  0.000
AMT*Solvent       -0.000325 -0.000163    0.000138   -1.17  0.257
BTA*AMT*Solvent    0.000308  0.000154    0.000138    1.11  0.281

Analysis of Variance for 48 (coded units)

Source               DF      Seq SS     Adj SS     Adj MS      F      P
Main Effects          3  0.00008610 0.00008610 0.00002870  62.50  0.000
2-Way Interactions    3  0.00001585 0.00001585 0.00000528  11.51  0.000
3-Way Interactions    1  0.00000057 0.00000057 0.00000057   1.24  0.281
Residual Error       16  0.00000735 0.00000735 0.00000046
  Pure Error         16  0.00000735 0.00000735 0.00000046
Total                23  0.00010987

Unusual Observations for 48

Obs         48        Fit  StDev Fit   Residual   St Resid
  4   0.005600   0.006767   0.000391  -0.001167      -2.11R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168 (coded units)

Term                Effect      Coef  StDev Coef       T      P
Constant                     0.006787    0.000111   61.35  0.000
BTA               -0.001042 -0.000521    0.000111   -4.71  0.000
AMT               -0.002458 -0.001229    0.000111  -11.11  0.000
Solvent           -0.000642 -0.000321    0.000111   -2.90  0.010
BTA*AMT           -0.001008 -0.000504    0.000111   -4.56  0.000
BTA*Solvent       -0.001092 -0.000546    0.000111   -4.93  0.000
AMT*Solvent       -0.000675 -0.000338    0.000111   -3.05  0.008
BTA*AMT*Solvent   -0.000058 -0.000029    0.000111   -0.26  0.795

Analysis of Variance for 168 (coded units)
```

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00004524	0.00004524	0.00001508	51.34	0.000
2-Way Interactions	3	0.00001598	0.00001598	0.00000533	18.14	0.000
3-Way Interactions	1	0.00000002	0.00000002	0.00000002	0.07	0.795
Residual Error	16	0.00000470	0.00000470	0.00000029		
Pure Error	16	0.00000470	0.00000470	0.00000029		
Total	23	0.00006595				

Estimated Effects and Coefficients for 504 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008317	0.000081	102.53	0.000
BTA	0.000033	0.000017	0.000081	0.21	0.840
AMT	-0.001183	-0.000592	0.000081	-7.29	0.000
Solvent	-0.000183	-0.000092	0.000081	-1.13	0.275
BTA*AMT	-0.000083	-0.000042	0.000081	-0.51	0.615
BTA*Solvent	-0.000317	-0.000158	0.000081	-1.95	0.069
AMT*Solvent	-0.000367	-0.000183	0.000081	-2.26	0.038
BTA*AMT*Solvent	0.000333	0.000167	0.000081	2.05	0.057

Analysis of Variance for 504 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00000861	0.00000861	0.00000287	18.17	0.000
2-Way Interactions	3	0.00000145	0.00000145	0.00000048	3.06	0.058
3-Way Interactions	1	0.00000067	0.00000067	0.00000067	4.22	0.057
Residual Error	16	0.00000253	0.00000253	0.00000016		
Pure Error	16	0.00000253	0.00000253	0.00000016		
Total	23	0.00001325				

Unusual Observations for 504

Obs	504	Fit	StDev Fit	Residual	St Resid
4	0.007700	0.008433	0.000229	-0.000733	-2.26R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008975	0.000101	89.13	0.000
BTA	0.000133	0.000067	0.000101	0.66	0.517
AMT	-0.000733	-0.000367	0.000101	-3.64	0.002
Solvent	-0.000217	-0.000108	0.000101	-1.08	0.298
BTA*AMT	0.000250	0.000125	0.000101	1.24	0.232
BTA*Solvent	-0.000567	-0.000283	0.000101	-2.81	0.012
AMT*Solvent	-0.000400	-0.000200	0.000101	-1.99	0.064
BTA*AMT*Solvent	0.000050	0.000025	0.000101	0.25	0.807

Analysis of Variance for 840 (coded units)

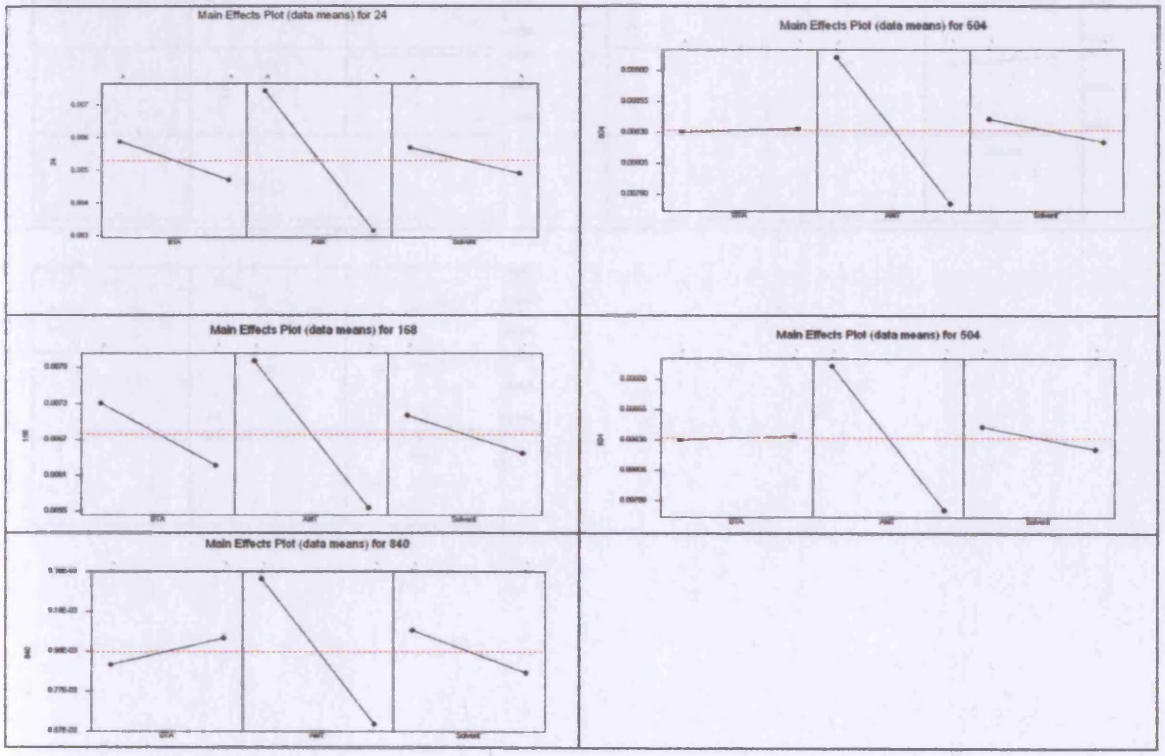
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00000362	0.00000362	0.00000121	4.95	0.013
2-Way Interactions	3	0.00000326	0.00000326	0.00000109	4.47	0.018
3-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.06	0.807
Residual Error	16	0.00000389	0.00000389	0.00000024		
Pure Error	16	0.00000389	0.00000389	0.00000024		
Total	23	0.00001079				

Unusual Observations for 840

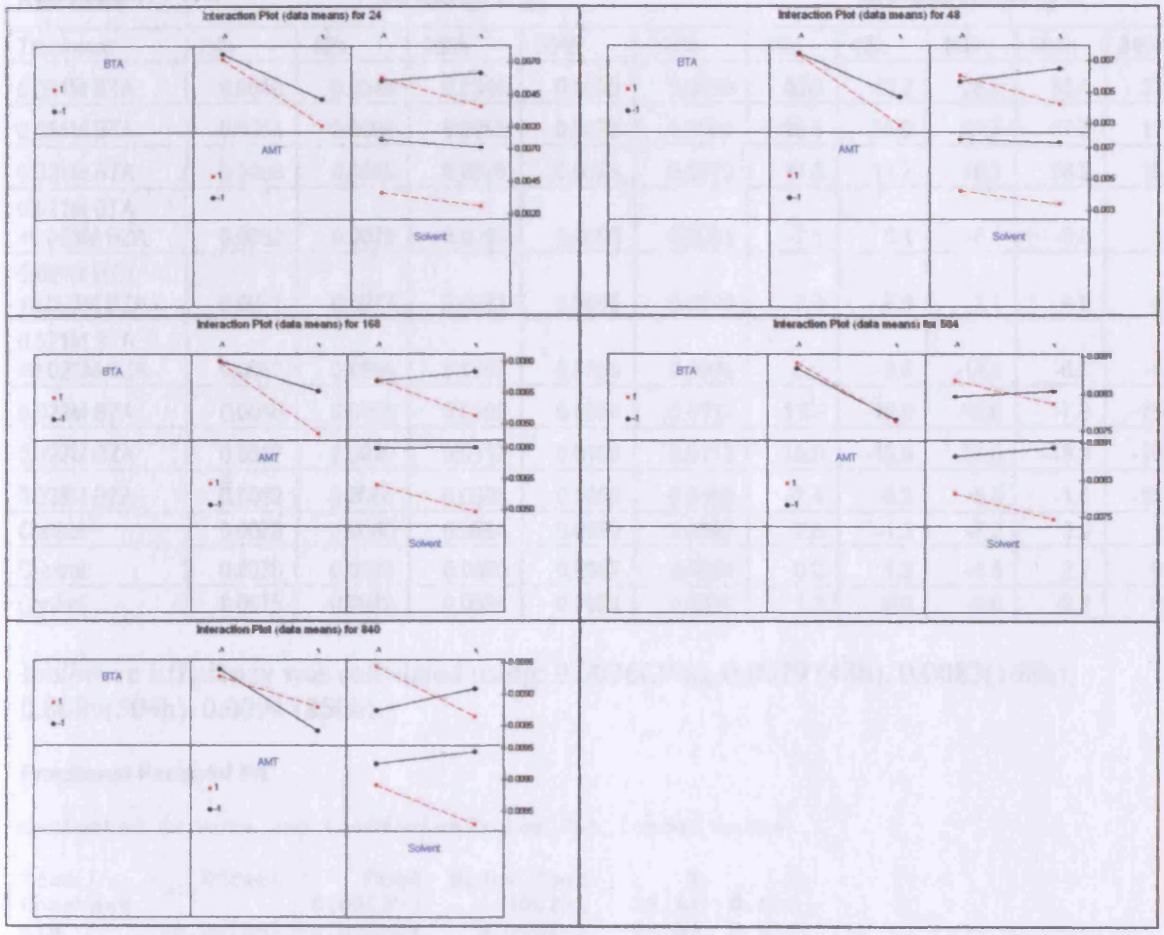
Obs	840	Fit	StDev Fit	Residual	St Resid

```
 23    0.007200    0.008467    0.000285  -0.001267      -3.14R
 24    0.009300    0.008467    0.000285   0.000833       2.07R

R denotes an observation with a large standardized residual

Alias Structure

I
BTA
AMT
Solvent
BTA*AMT
BTA*Solvent
AMT*Solvent
BTA*AMT*Solvent
```

Main Effect Plots



Interaction Plots



BTA + BZA 1	Wt change % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
0.021M BTA	0.0040	0.0040	0.0048	0.0059	0.0059	46.8	49.2	28.5	33.4	37.4
0.021M BTA	0.0064	0.0066	0.0059	0.0073	0.0083	16.1	16.6	11.7	17.7	11.9
0.021M BTA	0.0063	0.0065	0.0070	0.0075	0.0079	17.0	17.7	10.1	16.2	15.7
0.021M BTA +0.023M BZA	0.0082	0.0079	0.0093	0.0090	0.0093	-7.6	0.1	-8.1	-0.8	1.1
0.021M BTA +0.023M BZA	0.0071	0.0073	0.0081	0.0085	0.0090	7.0	7.9	-2.1	4.8	4.6
0.021M BTA +0.023M BZA	0.0082	0.0084	0.0097	0.0095	0.0098	-8.5	-6.6	-14.6	-6.8	-4.7
0.023M BZA	0.0086	0.0088	0.0103	0.0096	0.0112	-13.2	-10.9	-15.6	-7.8	-19.1
0.023M BZA	0.0087	0.0090	0.0117	0.0106	0.0113	-15.0	-13.6	-27.5	-18.9	-19.8
0.023M BZA	0.0082	0.0084	0.0086	0.0090	0.0109	-7.4	-6.2	-8.8	-1.5	-15.8
Control	0.0078	0.0080	0.0084	0.0089	0.0093	-2.6	-1.3	-7.2	0.0	1.1
Control	0.0076	0.0078	0.0080	0.0087	0.0094	0.0	1.3	-4.8	2.2	0.0
Control	0.0075	0.0079	0.0084	0.0091	0.0094	1.3	0.0	-9.6	-2.2	0.0

Inhibitive Efficiency was calculated using: 0.0076(24h), 0.0079 (48h), 0.0083(168h), 0.0089(504h), 0.0094 (850h).

Fractional Factorial Fit

```
Estimated Effects and Coefficients for 24h (coded units)

Term          Effect      Coef  StDev Coef       T      P
Constant                0.007383    0.000221   33.44  0.000
BTA       -0.001367 -0.000683    0.000221   -3.09  0.015
BZA        0.000700  0.000350    0.000221    1.59  0.152
BTA*BZA    0.001567  0.000783    0.000221    3.55  0.008

Analysis of Variance for 24h (coded units)

Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00000707  0.00000707  0.00000354   6.05  0.025
2-Way Interactions    1  0.00000736  0.00000736  0.00000736  12.59  0.008
Residual Error        8  0.00000468  0.00000468  0.00000059
  Pure Error          8  0.00000468  0.00000468  0.00000059
Total                11  0.00001912

Unusual Observations for 24h

Obs        24h        Fit  StDev Fit   Residual   St Resid
  4   0.004000   0.005567   0.000442  -0.001567      -2.51R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term          Effect      Coef  StDev Coef       T      P
Constant                0.007550    0.000232   32.59  0.000
BTA       -0.001533 -0.000767    0.000232   -3.31  0.011
```

BZA	0.000667	0.000333	0.000232	1.44	0.188
BTA*BZA	0.001500	0.000750	0.000232	3.24	0.012

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000839	0.00000839	0.00000419	6.51	0.021
2-Way Interactions	1	0.00000675	0.00000675	0.00000675	10.48	0.012
Residual Error	8	0.00000515	0.00000515	0.00000064		
Pure Error	8	0.00000515	0.00000515	0.00000064		
Total	11	0.00002029				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
4	0.004000	0.005700	0.000463	-0.001700	-2.59R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008350	0.000302	27.68	0.000
BTA	-0.001767	-0.000883	0.000302	-2.93	0.019
BZA	0.000600	0.000300	0.000302	0.99	0.349
BTA*BZA	0.002533	0.001267	0.000302	4.20	0.003

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001044	0.00001044	0.00000522	4.78	0.043
2-Way Interactions	1	0.00001925	0.00001925	0.00001925	17.64	0.003
Residual Error	8	0.00000873	0.00000873	0.00000109		
Pure Error	8	0.00000873	0.00000873	0.00000109		
Total	11	0.00003843				

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008633	0.000188	45.83	0.000
BTA	-0.001367	-0.000683	0.000188	-3.63	0.007
BZA	0.000633	0.000317	0.000188	1.68	0.131
BTA*BZA	0.001467	0.000733	0.000188	3.89	0.005

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000681	0.00000681	0.00000340	7.99	0.012
2-Way Interactions	1	0.00000645	0.00000645	0.00000645	15.15	0.005
Residual Error	8	0.00000341	0.00000341	0.00000043		
Pure Error	8	0.00000341	0.00000341	0.00000043		
Total	11	0.00001667				

Estimated Effects and Coefficients for 840h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.009308	0.000197	47.24	0.000
BTA	-0.001883	-0.000942	0.000197	-4.78	0.001
BZA	0.000117	0.000058	0.000197	0.30	0.775
BTA*BZA	0.001883	0.000942	0.000197	4.78	0.001

Analysis of Variance for 840h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001068	0.00001068	0.00000534	11.47	0.004
2-Way Interactions	1	0.00001064	0.00001064	0.00001064	22.84	0.001
Residual Error	8	0.00000373	0.00000373	0.00000047		
Pure Error	8	0.00000373	0.00000373	0.00000047		
Total	11	0.00002505				

Unusual Observations for 840h

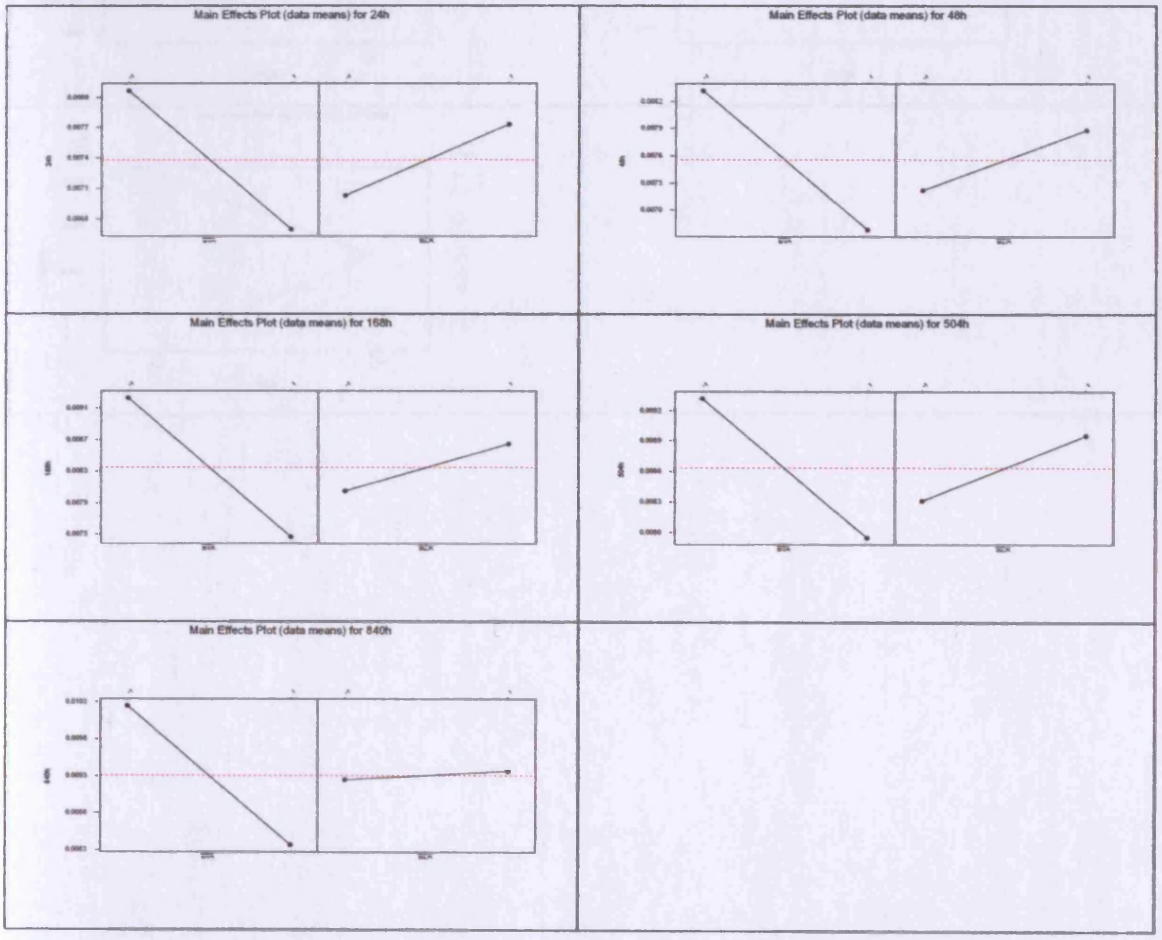
Obs	840h	Fit	StDev Fit	Residual	St Resid
4	0.005900	0.007367	0.000394	-0.001467	-2.63R

R denotes an observation with a large standardized residual

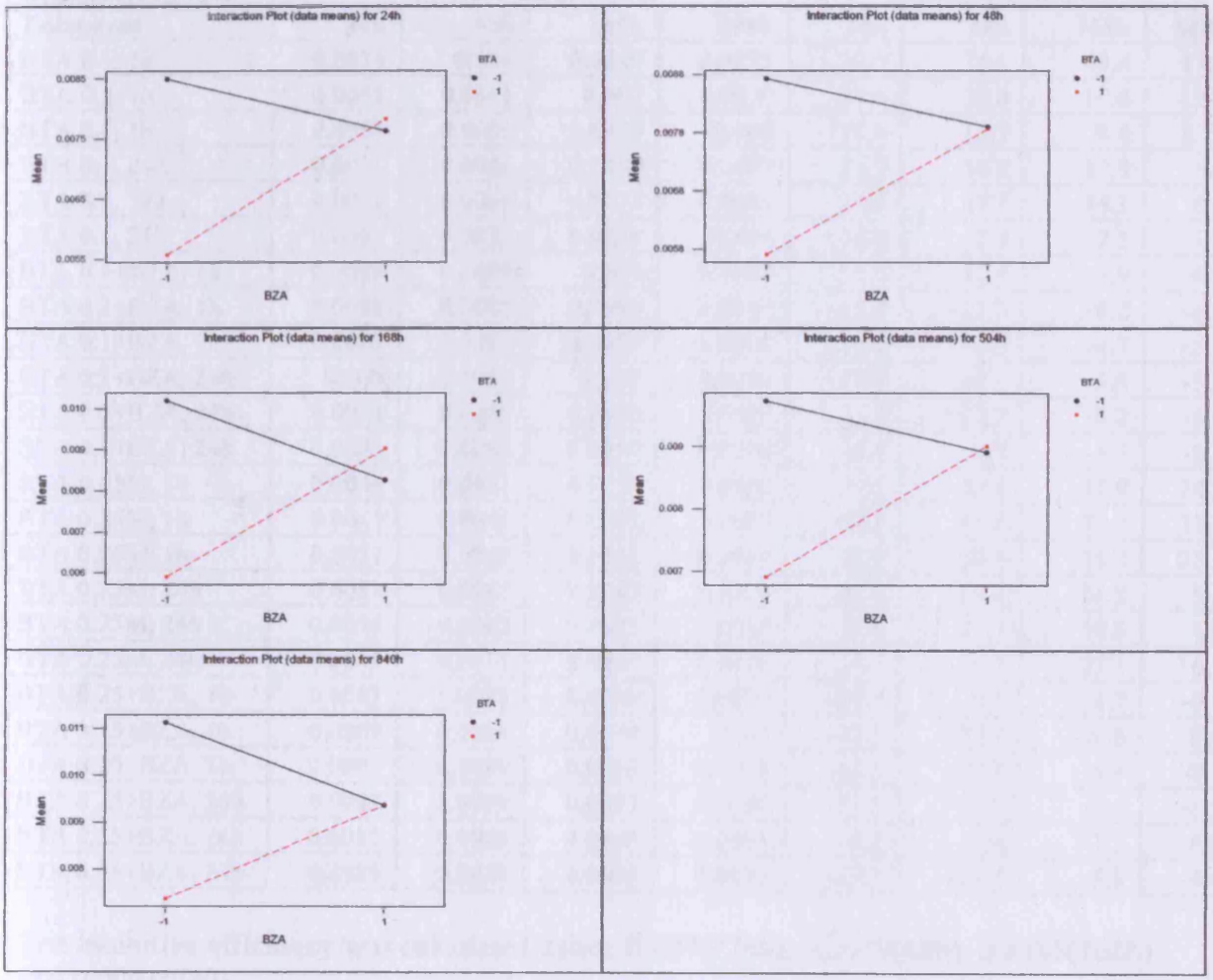
Alias Structure

I
BTA
BZA
BTA*BZA

Main Effect Plots



Interaction Plots



BTA + BZA 2	Weight changes % (g)				Inhibitive efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1, 1h	0.0056	0.006	0.0069	0.0075	26.3	24.1	18.8	17.6
BTA 0.1, 1h	0.0055	0.0061	0.007	0.0079	27.6	22.8	17.6	13.2
BTA 0.1, 1h	0.0062	0.0069	0.0077	0.008	18.4	12.7	9.4	12.1
BTA 0.1, 24h	0.0058	0.0066	0.0074	0.0087	23.7	16.5	12.9	4.4
BTA 0.1, 24h	0.0058	0.0065	0.0073	0.0085	23.7	17.7	14.1	6.6
BTA 0.1, 24h	0.0067	0.0072	0.0079	0.009	11.8	8.9	7.1	1.1
BTA 0.1+BZA, 1h	0.0088	0.0088	0.009	0.0097	-15.8	-11.4	-5.9	-6.6
BTA 0.1+BZA, 1h	0.0088	0.0089	0.0092	0.0097	-15.8	-12.7	-8.2	-6.6
BTA 0.1+BZA, 1h	0.0083	0.0084	0.0089	0.0096	-9.2	-6.3	-4.7	-5.5
BTA 0.1+BZA, 24h	0.009	0.0087	0.009	0.0094	-18.4	-10.1	-5.9	-3.3
BTA 0.1+BZA, 24h	0.0088	0.0089	0.0092	0.0097	-15.8	-12.7	-8.2	-6.6
BTA 0.1+BZA, 24h	0.0083	0.0084	0.0089	0.0096	-9.2	-6.3	-4.7	-5.5
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.9	24.2
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.007	42.1	39.2	35.3	23.1
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	28.2	25.3
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	21.2	5.5
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	16.5	6.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	27.1	16.5
BTA 0.25+BZA, 1h	0.0087	0.0083	0.0089	0.0095	-14.5	-5.1	-4.7	-4.4
BTA 0.25+BZA, 1h	0.0089	0.0089	0.0094	0.01	-17.1	-12.7	-10.6	-9.9
BTA 0.25+BZA, 1h	0.0087	0.0089	0.0093	0.0098	-14.5	-12.7	-9.4	-7.7
BTA 0.25+BZA, 24h	0.0092	0.0089	0.0093	0.0096	-21.1	-12.7	-9.4	-5.5
BTA 0.25+BZA, 24h	0.0083	0.0085	0.0088	0.0091	-9.2	-7.6	-3.5	0.0
BTA 0.25+BZA, 24h	0.0089	0.0088	0.0092	0.0095	-17.1	-11.4	-8.2	-4.4

The inhibitive efficiency was calculated using: 0.0076(24h), 0.0079(48h), 0.0085(168h) and 0.0091(840).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007092	0.000074	96.20	0.000
BTA	-0.000417	-0.000208	0.000074	-2.83	0.012
BZA	0.003267	0.001633	0.000074	22.16	0.000
Immersio	0.000200	0.000100	0.000074	1.36	0.194
BTA*BZA	0.000533	0.000267	0.000074	3.62	0.002
BTA*Immersio	-0.000000	-0.000000	0.000074	-0.00	1.000
BZA*Immersio	-0.000150	-0.000075	0.000074	-1.02	0.324
BTA*BZA*Immersio	-0.000017	-0.000008	0.000074	-0.11	0.911

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00006531	0.00006531	0.00002177	166.92	0.000
2-Way Interactions	3	0.00000184	0.00000184	0.00000061	4.71	0.015
3-Way Interactions	1	0.00000000	0.00000000	0.00000000	0.01	0.911
Residual Error	16	0.00000209	0.00000209	0.00000013		
Pure Error	16	0.00000209	0.00000209	0.00000013		
Total	23	0.00006924				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
18	0.006700	0.006100	0.000208	0.000600	2.03R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007358	0.000079	92.69	0.000
BTA	-0.000517	-0.000258	0.000079	-3.25	0.005
BZA	0.002683	0.001342	0.000079	16.90	0.000
Immersio	0.000283	0.000142	0.000079	1.78	0.093
BTA*BZA	0.000550	0.000275	0.000079	3.46	0.003
BTA*Immersio	0.000083	0.000042	0.000079	0.52	0.607
BZA*Immersio	-0.000283	-0.000142	0.000079	-1.78	0.093
BTA*BZA*Immersio	-0.000050	-0.000025	0.000079	-0.31	0.757

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00004529	0.00004529	0.00001510	99.80	0.000
2-Way Interactions	3	0.00000234	0.00000234	0.00000078	5.15	0.011
3-Way Interactions	1	0.00000001	0.00000001	0.00000001	0.10	0.757
Residual Error	16	0.00000242	0.00000242	0.00000015		
Pure Error	16	0.00000242	0.00000242	0.00000015		
Total	23	0.00005006				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
23	0.005100	0.005833	0.000225	-0.000733	-2.31R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007942	0.000064	124.87	0.000
BTA	-0.000517	-0.000258	0.000064	-4.06	0.001
BZA	0.002300	0.001150	0.000064	18.08	0.000
Immersio	0.000283	0.000142	0.000064	2.23	0.041
BTA*BZA	0.000633	0.000317	0.000064	4.98	0.000
BTA*Immersio	0.000117	0.000058	0.000064	0.92	0.373
BZA*Immersio	-0.000333	-0.000167	0.000064	-2.62	0.019
BTA*BZA*Immersio	-0.000167	-0.000083	0.000064	-1.31	0.209

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003382	0.00003382	0.00001127	116.13	0.000
2-Way Interactions	3	0.00000316	0.00000316	0.00000105	10.83	0.000
3-Way Interactions	1	0.00000017	0.00000017	0.00000017	1.72	0.209
Residual Error	16	0.00000155	0.00000155	0.00000010		
Pure Error	16	0.00000155	0.00000155	0.00000010		
Total	23	0.00003870				

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008758	0.000056	155.81	0.000
BTA	-0.000367	-0.000183	0.000056	-3.26	0.005
BZA	0.001683	0.000842	0.000056	14.97	0.000

Immersio	0.000450	0.000225	0.000056	4.00	0.001
BTA*BZA	0.000333	0.000167	0.000056	2.96	0.009
BTA*Immersio	0.000033	0.000017	0.000056	0.30	0.771
BZA*Immersio	-0.000683	-0.000342	0.000056	-6.08	0.000
BTA*BZA*Immersion	-0.000167	-0.000083	0.000056	-1.48	0.158

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001902	0.00001902	0.00000634	83.62	0.000
2-Way Interactions	3	0.00000348	0.00000348	0.00000116	15.27	0.000
3-Way Interactions	1	0.00000017	0.00000017	0.00000017	2.20	0.158
Residual Error	16	0.00000121	0.00000121	0.00000008		
Pure Error	16	0.00000121	0.00000121	0.00000008		
Total	23	0.00002388				

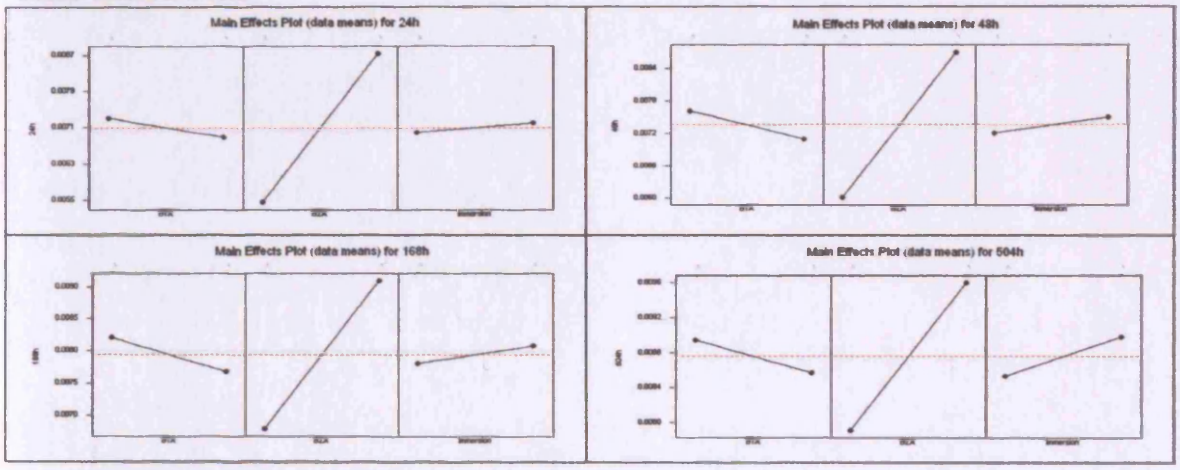
Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid
23	0.007600	0.008233	0.000159	-0.000633	-2.82R

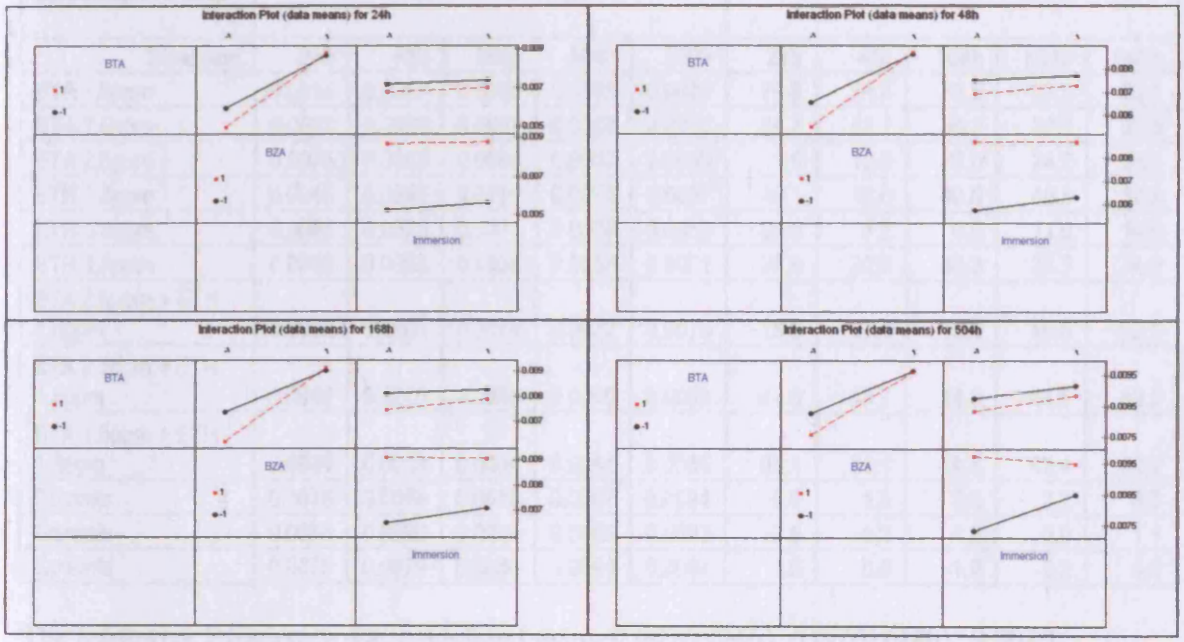
R denotes an observation with a large standardized residual

Alias Structure
I
BTA
BZA
Immersion
BTA*BZA
BTA*Immersion
BZA*Immersion
BTA*BZA*Immersion

Main Effects Plots



Interaction Plots



BTA + ETH 1	Weight Change % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 2.5ppm	0.0015	0.0067	0.0056	0.0060	0.0073	79.8	14.6	32.5	33.0	22.1
BTA 2.5ppm	0.0012	0.0031	0.0051	0.0058	0.0062	84.7	61.1	38.2	34.8	34.5
BTA 2.5ppm	0.0075	0.0063	0.0066	0.0067	0.0069	1.9	19.9	20.0	24.2	26.5
ETH 1.8ppm	0.0045	0.0046	0.0050	0.0053	0.0057	40.1	42.0	40.0	40.3	38.9
ETH 1.8ppm	0.0096	0.0073	0.0077	0.0078	0.0080	-25.8	7.2	6.6	11.9	14.8
ETH 1.8ppm	0.0055	0.0053	0.0056	0.0058	0.0061	27.8	32.6	32.3	34.3	34.9
BTA 2.5ppm + ETH 1.8ppm	0.0062	0.0065	0.0070	0.0072	0.0073	18.6	17.7	16.3	19.6	22.1
BTA 2.5ppm + ETH 1.8ppm	0.0040	0.0040	0.0046	0.0049	0.0056	47.5	48.7	44.3	44.5	40.2
BTA 2.5ppm + ETH 1.8ppm	0.0004	0.0039	0.0046	0.0051	0.0056	95.1	51.1	44.4	42.4	40.8
Controls	0.0076	0.0078	0.0080	0.0087	0.0094	0.0	1.3	3.6	2.2	0.0
Controls	0.0078	0.0080	0.0084	0.0089	0.0093	-2.6	-1.3	-1.2	0.0	1.1
Controls	0.0075	0.0079	0.0084	0.0091	0.0094	1.3	0.0	-1.2	-2.2	0.0

The Inhibitive Efficiency was calculated using 0.0076 (24h), 0.0079 (48h), 0.0083 (168h), 0.0089 (504h) and 0.0094 (840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.005275	0.000771	6.84	0.000
BTA	-0.003617	-0.001808	0.000771	-2.35	0.047
ETH	-0.000483	-0.000242	0.000771	-0.31	0.762
BTA*ETH	0.000617	0.000308	0.000771	0.40	0.700

Analysis of Variance for 24 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00003994	0.00003994	0.00001997	2.80	0.120
2-Way Interactions	1	0.00000114	0.00000114	0.00000114	0.16	0.700
Residual Error	8	0.00005706	0.00005706	0.00000713		
Pure Error	8	0.00005706	0.00005706	0.00000713		
Total	11	0.00009814				

Estimated Effects and Coefficients for 48 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.005950	0.000409	14.54	0.000
BTA	-0.001733	-0.000867	0.000409	-2.12	0.067
ETH	-0.001367	-0.000683	0.000409	-1.67	0.133
BTA*ETH	0.000800	0.000400	0.000409	0.98	0.357

Analysis of Variance for 48 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001462	0.00001462	0.00000731	3.64	0.075
2-Way Interactions	1	0.00000192	0.00000192	0.00000192	0.96	0.357
Residual Error	8	0.00001607	0.00001607	0.00000201		

Pure Error	8	0.00001607	0.00001607	0.00000201	
Total	11	0.00003261			

Estimated Effects and Coefficients for 168 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006383	0.000308	20.70	0.000
BTA	-0.001600	-0.000800	0.000308	-2.59	0.032
ETH	-0.001267	-0.000633	0.000308	-2.05	0.074
BTA*ETH	0.000900	0.000450	0.000308	1.46	0.183

Analysis of Variance for 168 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001249	0.00001249	0.00000625	5.47	0.032
2-Way Interactions	1	0.00000243	0.00000243	0.00000243	2.13	0.183
Residual Error	8	0.00000913	0.00000913	0.00000114		
Pure Error	8	0.00000913	0.00000913	0.00000114		
Total	11	0.00002406				

Estimated Effects and Coefficients for 504 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006642	0.000325	20.42	0.000
BTA	-0.001917	-0.000958	0.000325	-2.95	0.019
ETH	-0.001250	-0.000625	0.000325	-1.92	0.091
BTA*ETH	0.001350	0.000675	0.000325	2.08	0.072

Analysis of Variance for 504 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001571	0.00001571	0.00000785	6.19	0.024
2-Way Interactions	1	0.00000547	0.00000547	0.00000547	4.31	0.072
Residual Error	8	0.00001015	0.00001015	0.00000127		
Pure Error	8	0.00001015	0.00001015	0.00000127		
Total	11	0.00003133				

Estimated Effects and Coefficients for 840 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007117	0.000299	23.83	0.000
BTA	-0.001733	-0.000867	0.000299	-2.90	0.020
ETH	-0.001467	-0.000733	0.000299	-2.46	0.040
BTA*ETH	0.001300	0.000650	0.000299	2.18	0.061

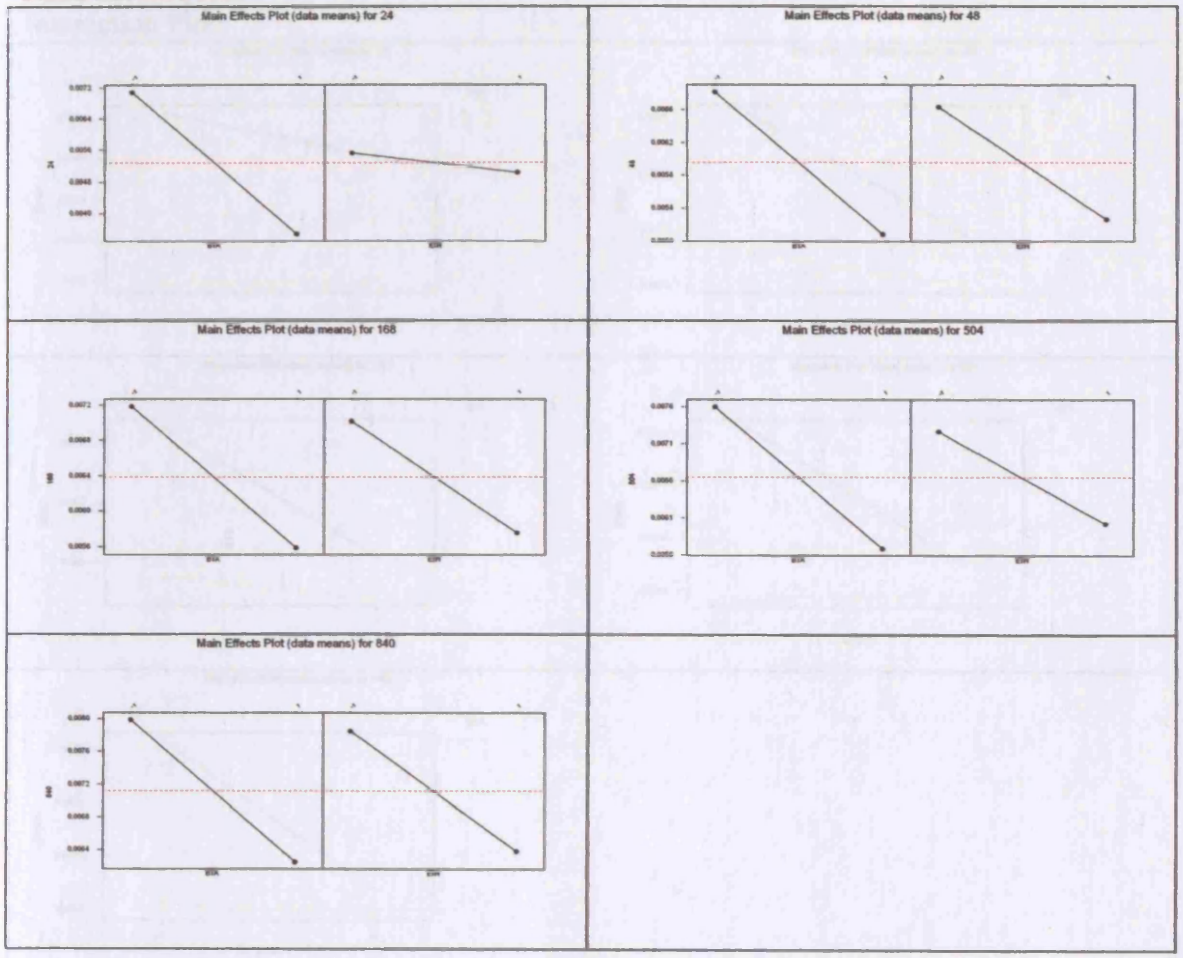
Analysis of Variance for 840 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001547	0.00001547	0.00000773	7.23	0.016
2-Way Interactions	1	0.00000507	0.00000507	0.00000507	4.74	0.061
Residual Error	8	0.00000856	0.00000856	0.00000107		
Pure Error	8	0.00000856	0.00000856	0.00000107		
Total	11	0.00002910				

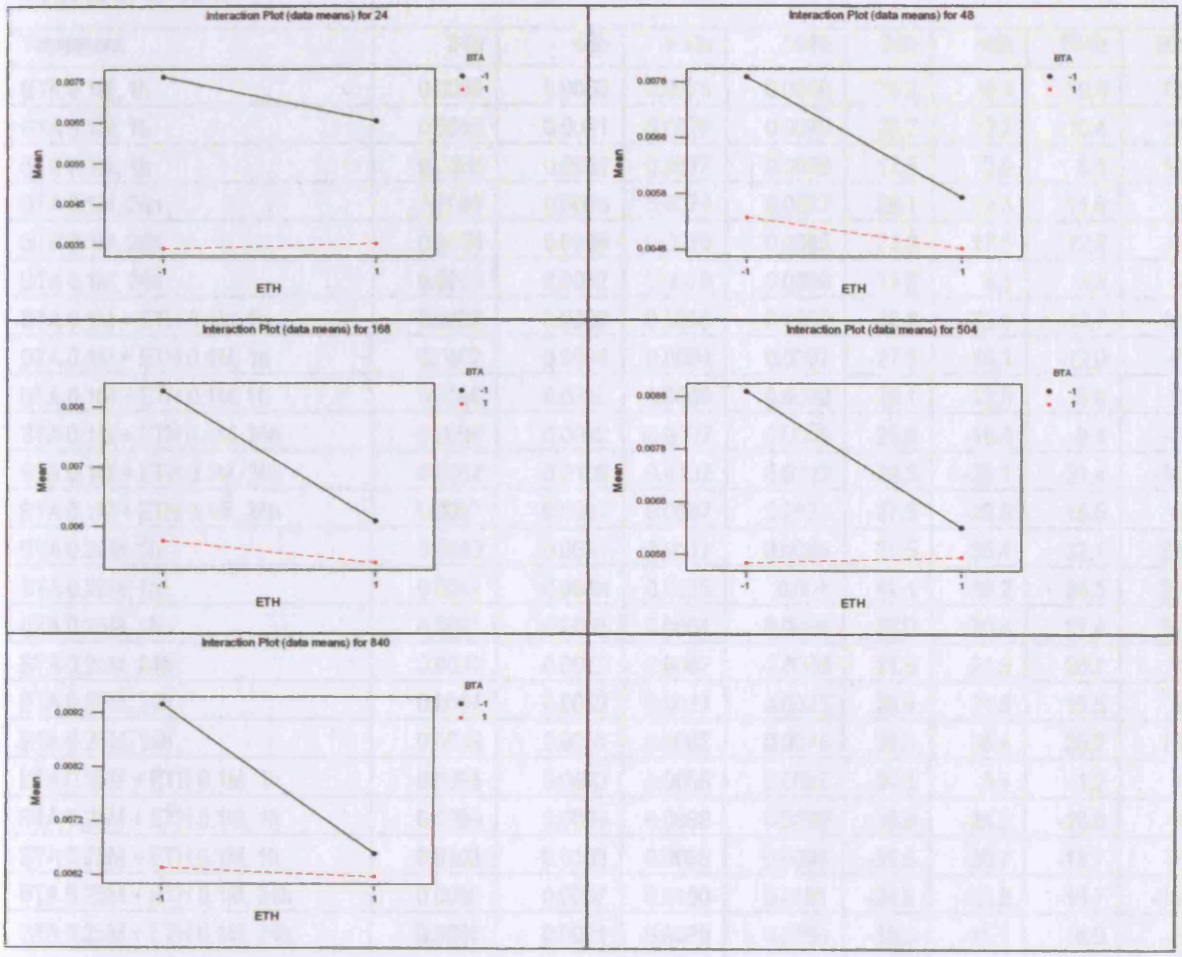
Alias Structure

-
BTA
ETH
BTA*ETH

Main Effect Plots



Interaction Plots



BTA +ETH 2	Weight Change % (g)				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M, 1h	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M, 1h	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M, 1h	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M, 24h	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M, 24h	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M, 24h	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M + ETH 0.1M, 1h	0.0100	0.0099	0.0099	0.0102	-32.2	-25.1	-17.7	-13.4
BTA 0.1M + ETH 0.1M, 1h	0.0097	0.0094	0.0094	0.0097	-27.3	-19.1	-12.0	-7.5
BTA 0.1M + ETH 0.1M, 1h	0.0098	0.0089	0.0089	0.0090	-29.1	-12.6	-5.9	0.1
BTA 0.1M + ETH 0.1M, 24h	0.0096	0.0092	0.0092	0.0095	-25.8	-16.4	-9.4	-5.9
BTA 0.1M + ETH 0.1M, 24h	0.0102	0.0102	0.0102	0.0103	-34.3	-29.1	-21.4	-14.9
BTA 0.1M + ETH 0.1M, 24h	0.0097	0.0097	0.0097	0.2979	-27.5	-22.8	-15.5	-10
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.007	42.1	39.2	34.5	22.2
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M + ETH 0.1M, 1h	0.0095	0.0083	0.0085	0.0087	-24.5	-5.4	-1.2	3.8
BTA 0.25M + ETH 0.1M, 1h	0.0099	0.0099	0.0098	0.0099	-30.8	-25.3	-16.8	-9.7
BTA 0.25M + ETH 0.1M, 1h	0.0103	0.0103	0.0095	0.0094	-35.5	-30.7	-13.7	-4.6
BTA 0.25M + ETH 0.1M, 24h	0.0095	0.0097	0.0100	0.0101	-24.9	-22.6	-18.7	-11.8
BTA 0.25M + ETH 0.1M, 24h	0.0090	0.0091	0.0089	0.0093	-19.0	-15.1	-6.0	-3.1
BTA 0.25M + ETH 0.1M, 24h	0.0096	0.0096	0.0099	0.0094	-26.3	-21.5	-17.8	-4.3

The Inhibitive Efficiency was calculated using: 0.0076(24h), 0.0079(48h), 0.0084(168h) and 0.0090(504h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007596	0.000072	105.43	0.000
BTA	-0.000575	-0.000287	0.000072	-3.99	0.001
ETH	0.004275	0.002138	0.000072	29.67	0.000
immersio	0.000042	0.000021	0.000072	0.29	0.776
BTA*ETH	0.000375	0.000187	0.000072	2.60	0.019
BTA*immersio	-0.000125	-0.000063	0.000072	-0.87	0.399
ETH*immersio	-0.000308	-0.000154	0.000072	-2.14	0.048
BTA*ETH*immersio	-0.000142	-0.000071	0.000072	-0.98	0.340

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00011165	0.00011165	0.00003722	298.72	0.000

2-Way Interactions	3	0.00000151	0.00000151	0.00000050	4.03	0.026
3-Way Interactions	1	0.00000012	0.00000012	0.00000012	0.97	0.340
Residual Error	16	0.00000199	0.00000199	0.00000012		
Pure Error	16	0.00000199	0.00000199	0.00000012		
Total	23	0.00011527				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
15	0.006700	0.006100	0.000204	0.000600	2.08R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007767	0.000117	66.28	0.000
BTA	-0.000567	-0.000283	0.000117	-2.42	0.028
ETH	0.003500	0.001750	0.000117	14.93	0.000
immersio	0.000350	0.000175	0.000117	1.49	0.155
BTA*ETH	0.000500	0.000250	0.000117	2.13	0.049
BTA*immersio	-0.000017	-0.000008	0.000117	-0.07	0.944
ETH*immersio	-0.000217	-0.000108	0.000117	-0.92	0.369
BTA*ETH*immersio	-0.000150	-0.000075	0.000117	-0.64	0.531

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00007616	0.00007616	0.00002539	77.03	0.000
2-Way Interactions	3	0.00000178	0.00000178	0.00000059	1.80	0.187
3-Way Interactions	1	0.00000014	0.00000014	0.00000014	0.41	0.531
Residual Error	16	0.00000527	0.00000527	0.00000033		
Pure Error	16	0.00000527	0.00000527	0.00000033		
Total	23	0.00008335				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
4	0.008300	0.009500	0.000331	-0.001200	-2.56R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008167	0.000099	82.90	0.000
BTA	-0.000683	-0.000342	0.000099	-3.47	0.003
ETH	0.002650	0.001325	0.000099	13.45	0.000
immersio	0.000417	0.000208	0.000099	2.11	0.050
BTA*ETH	0.000567	0.000283	0.000099	2.88	0.011
BTA*immersio	0.000200	0.000100	0.000099	1.02	0.325
ETH*immersio	-0.000100	-0.000050	0.000099	-0.51	0.619
BTA*ETH*immersio	-0.000183	-0.000092	0.000099	-0.93	0.366

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00004598	0.00004598	0.00001533	65.80	0.000
2-Way Interactions	3	0.00000223	0.00000223	0.00000074	3.19	0.052
3-Way Interactions	1	0.00000020	0.00000020	0.00000020	0.87	0.366
Residual Error	16	0.00000373	0.00000373	0.00000023		
Pure Error	16	0.00000373	0.00000373	0.00000023		
Total	23	0.00005213				

Estimated Effects and Coefficients for 504h (coded units)

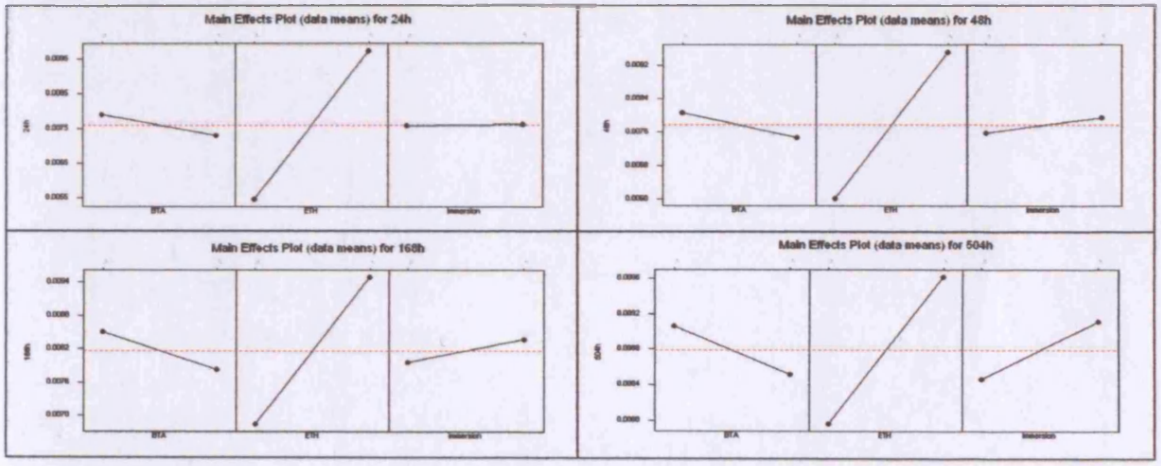
Term	Effect	Coef	StDev Coef	T	P
Constant		0.008788	0.000087	100.89	0.000
BTA	-0.000542	-0.000271	0.000087	-3.11	0.007
ETH	0.001658	0.000829	0.000087	9.52	0.000
immersio	0.000658	0.000329	0.000087	3.78	0.002
BTA*ETH	0.000242	0.000121	0.000087	1.39	0.184
BTA*immersio	0.000142	0.000071	0.000087	0.81	0.428
ETH*immersio	-0.000392	-0.000196	0.000087	-2.25	0.039
BTA*ETH*immersio	-0.000142	-0.000071	0.000087	-0.81	0.428

Analysis of Variance for 504h (coded units)

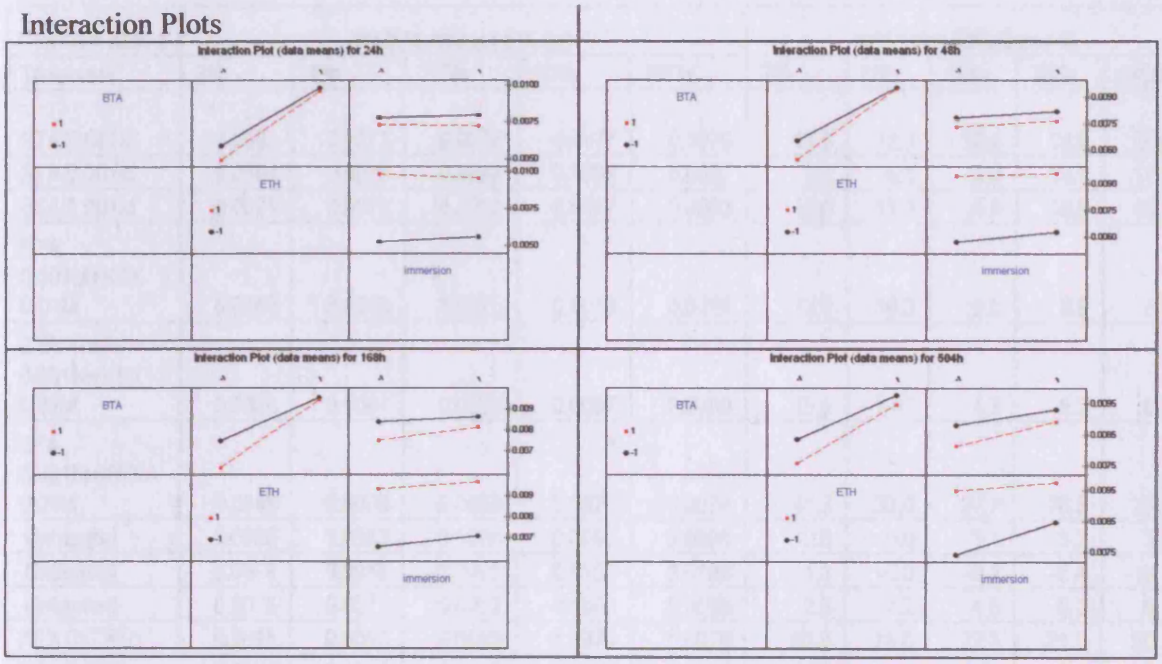
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00002086	0.00002086	0.00000695	38.19	0.000
2-Way Interactions	3	0.00000139	0.00000139	0.00000046	2.55	0.092
3-Way Interactions	1	0.00000012	0.00000012	0.00000012	0.66	0.428
Residual Error	16	0.00000291	0.00000291	0.00000018		
Pure Error	16	0.00000291	0.00000291	0.00000018		
Total	23	0.00002529				

Alias Structure
I
BTA
ETH
immersion
BTA*ETH
BTA*immersion
ETH*immersion
BTA*ETH*immersion

Main Effect Plots



Interaction Plots



BTA + KEX 1	Weight changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.001M	0.0094	0.0073	0.0078	0.0077	0.0079	12.6	12.3	10.4	19.2	20.5
BTA 0.001M	0.0104	0.0079	0.0082	0.0083	0.0087	3.4	5.1	5.3	13.1	11.9
BTA 0.001M	0.0070	0.0074	0.0082	0.0077	0.0083	13.0	11.3	5.6	18.8	16.5
BTA 0.001M+KEX 0.01M	0.0068	0.0068	0.0079	0.0088	0.0094	12.9	18.3	9.0	6.9	5.0
BTA 0.001M+KEX 0.01M	0.0066	0.0067	0.0083	0.0087	0.0090	15.8	18.7	4.7	8.3	8.9
BTA 0.001M+KEX 0.01M	0.0046	0.0050	0.0063	0.0070	0.0074	41.3	39.6	27.7	26.3	25.1
Untreated	0.0080	0.0083	0.0086	0.0092	0.0096	-2.6	0.0	1.1	3.2	3.0
Untreated	0.0079	0.0088	0.0095	0.0103	0.0109	-1.3	-6.0	-9.2	-8.4	-10.1
Untreated	0.0076	0.0077	0.0083	0.0089	0.0093	2.6	7.2	4.6	6.3	6.1
KEX 0.01M	0.0045	0.0051	0.0068	0.0074	0.0079	42.8	38.6	22.3	21.9	20.3
KEX 0.01M	0.0054	0.0057	0.0072	0.0078	0.0083	31.3	31.3	17.1	17.4	16.7
KEX 0.01M	0.0053	0.0056	0.0066	0.0069	0.0073	32.3	32.8	23.7	27.0	26.7

The inhibitive efficiency was calculated using: 0.0078(24h), 0.0083(48h), 0.0087(168h), 0.0095(504h) and 0.0099(840h)
These values are the average values of the untreated coupons of the experiment.

Fractional Factorial Fit

```
Estimated Effects and Coefficients for 24h (coded units)

Term          Effect      Coef  StDev Coef       T      P
Constant                0.006483    0.000201   32.33  0.000
BTA         0.000067  0.000033    0.000201    0.17  0.872
KEX        -0.001900 -0.000950    0.000201   -4.74  0.001
BTA*KEX     0.000867  0.000433    0.000201    2.16  0.063

Analysis of Variance for 24h (coded units)

Source                DF       Seq SS      Adj SS      Adj MS      F      P
Main Effects           2  0.00001084  0.00001084  0.00000542  11.24  0.005
2-Way Interactions     1  0.00000225  0.00000225  0.00000225   4.67  0.063
Residual Error         8  0.00000386  0.00000386  0.00000048
  Pure Error           8  0.00000386  0.00000386  0.00000048
Total                 11  0.00001696

Unusual Observations for 24h

Obs        24h         Fit  StDev Fit    Residual    St Resid
 12   0.004600    0.006000   0.000401  -0.001400       -2.47R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)
```

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006858	0.000179	38.37	0.000
BTA	-0.000017	-0.000008	0.000179	-0.05	0.964
KEX	-0.002083	-0.001042	0.000179	-5.83	0.000
BTA*KEX	0.000717	0.000358	0.000179	2.00	0.080

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00001302	0.00001302	0.00000651	16.98	0.001
2-Way Interactions	1	0.00000154	0.00000154	0.00000154	4.02	0.080
Residual Error	8	0.00000307	0.00000307	0.00000038		
Pure Error	8	0.00000307	0.00000307	0.00000038		
Total	11	0.00001763				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
12	0.005000	0.006167	0.000357	-0.001167	-2.31R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007808	0.000186	42.03	0.000
BTA	-0.000050	-0.000025	0.000186	-0.13	0.896
KEX	-0.001250	-0.000625	0.000186	-3.36	0.010
BTA*KEX	0.000683	0.000342	0.000186	1.84	0.103

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000469	0.00000469	0.00000235	5.67	0.029
2-Way Interactions	1	0.00000140	0.00000140	0.00000140	3.38	0.103
Residual Error	8	0.00000331	0.00000331	0.00000041		
Pure Error	8	0.00000331	0.00000331	0.00000041		
Total	11	0.00000941				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
12	0.006300	0.007500	0.000372	-0.001200	-2.28R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008225	0.000198	41.45	0.000
BTA	-0.000383	-0.000192	0.000198	-0.97	0.362
KEX	-0.000917	-0.000458	0.000198	-2.31	0.050
BTA*KEX	0.001183	0.000592	0.000198	2.98	0.018

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000296	0.00000296	0.00000148	3.13	0.099
2-Way Interactions	1	0.00000420	0.00000420	0.00000420	8.89	0.018
Residual Error	8	0.00000378	0.00000378	0.00000047		
Pure Error	8	0.00000378	0.00000378	0.00000047		
Total	11	0.00001094				

Unusual Observations for 504h

Obs	504h	Fit	StDev Fit	Residual	St Resid
12	0.007000	0.008167	0.000397	-0.001167	-2.08R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840h (coded units)

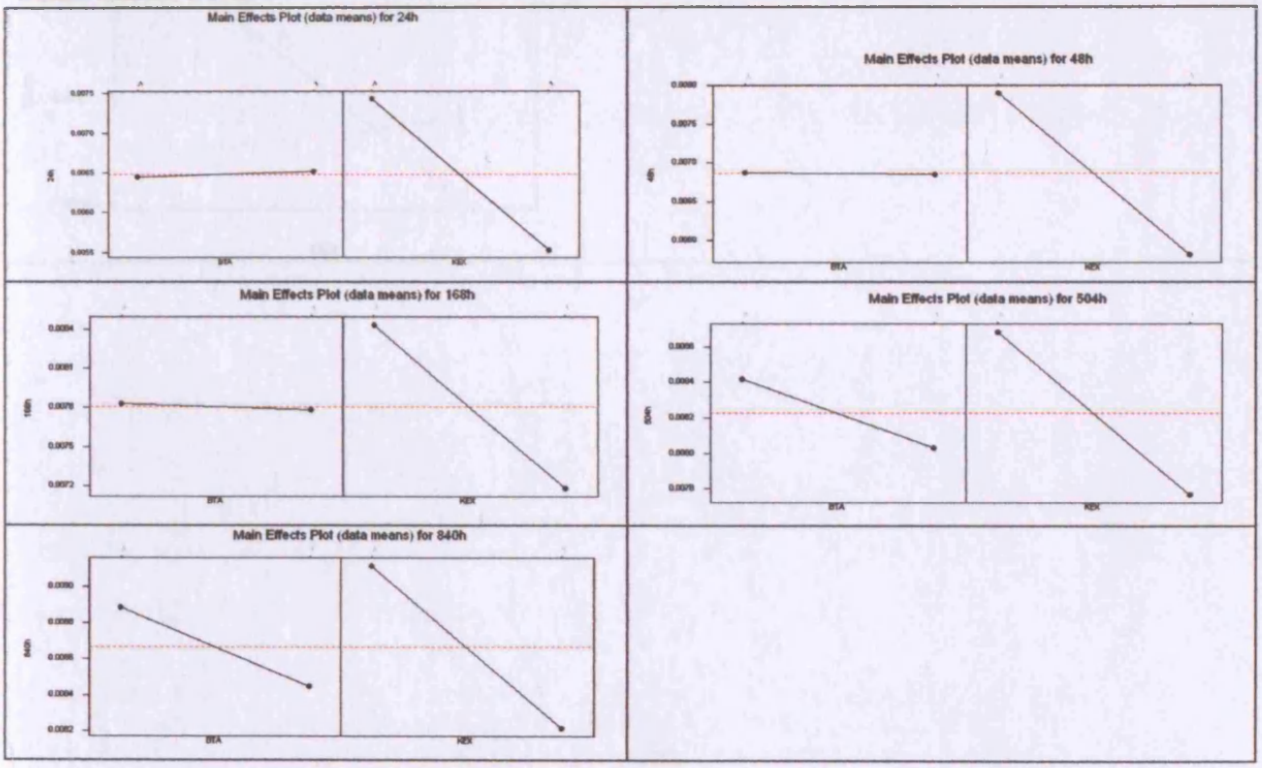
Term	Effect	Coef	StDev Coef	T	P
Constant		0.008667	0.000217	39.97	0.000
BTA	-0.000433	-0.000217	0.000217	-1.00	0.347
KEX	-0.000900	-0.000450	0.000217	-2.08	0.072
BTA*KEX	0.001200	0.000600	0.000217	2.77	0.024

Analysis of Variance for 840h (coded units)

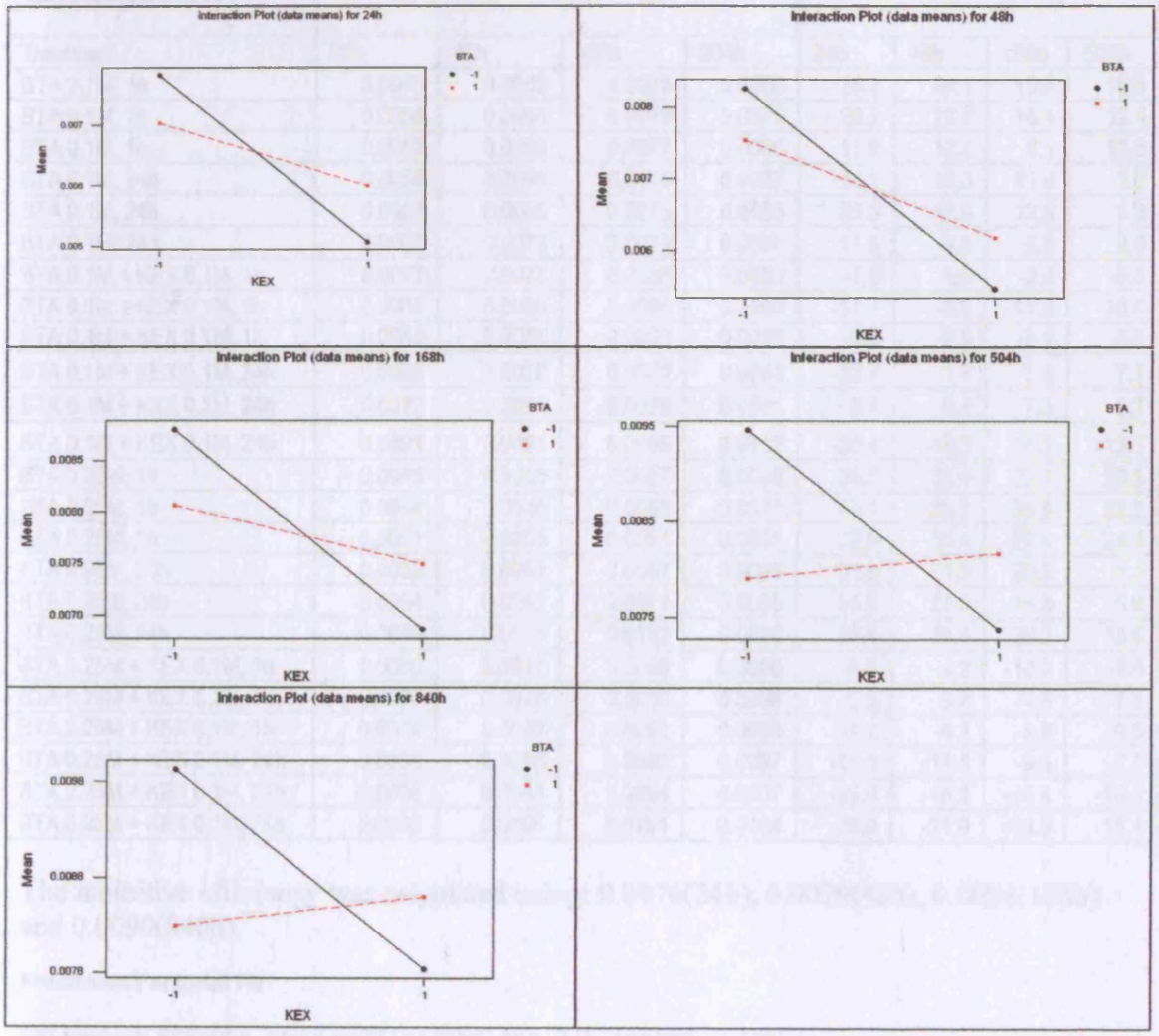
Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000299	0.00000299	0.00000150	2.65	0.131
2-Way Interactions	1	0.00000432	0.00000432	0.00000432	7.66	0.024
Residual Error	8	0.00000451	0.00000451	0.00000056		
Pure Error	8	0.00000451	0.00000451	0.00000056		
Total	11	0.00001183				

Alias Structure
I
BTA
KEX
BTA*KEX

Main Effect Plots



Interaction Plots



BTA + KEX 2	Weight Change % (g)				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M, 1h	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M, 1h	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M, 1h	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M, 24h	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M, 24h	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M, 24h	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M + KEX 0.1M, 1h	0.0077	0.0078	0.0086	0.0090	-1.6	1.5	-2.4	-0.5
BTA 0.1M + KEX 0.1M, 1h	0.0085	0.0086	0.0094	0.0100	-11.7	-8.9	-11.9	-10.6
BTA 0.1M + KEX 0.1M, 1h	0.0083	0.0085	0.0091	0.0096	-9.6	-8.0	-8.4	-6.9
BTA 0.1M + KEX 0.1M, 24h	0.0086	0.0078	0.0081	0.0083	-13.7	1.7	3.6	7.7
BTA 0.1M + KEX 0.1M, 24h	0.0072	0.0071	0.0078	0.0081	5.4	9.5	7.3	9.7
BTA 0.1M + KEX 0.1M, 24h	0.0091	0.0091	0.0096	0.0102	-20.4	-15.3	-14.1	-13.3
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.0070	42.1	39.2	34.5	22.2
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M + KEX 0.1M, 1h	0.0080	0.0082	0.0093	0.0098	-5.6	-4.2	-10.2	-9.0
BTA 0.25M + KEX 0.1M, 1h	0.0074	0.0076	0.0086	0.0096	2.6	3.7	-1.8	-7.1
BTA 0.25M + KEX 0.1M, 1h	0.0079	0.0082	0.0091	0.0099	-4.2	-4.2	-8.8	-9.5
BTA 0.25M + KEX 0.1M, 24h	0.0088	0.0088	0.0092	0.0097	-15.3	-11.4	-9.6	-7.5
BTA 0.25M + KEX 0.1M, 24h	0.0096	0.0093	0.0096	0.0107	-26.0	-18.1	-14.4	-18.5
BTA 0.25M + KEX 0.1M, 24h	0.0096	0.0096	0.0101	0.0104	-26.9	-21.9	-20.0	-15.1

The inhibitive efficiency was calculated using: 0.0076(24h), 0.0079(48h), 0.0084(168h) and 0.0090(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006925	0.000104	66.75	0.000
BTA	-0.000317	-0.000158	0.000104	-1.53	0.147
KEX	0.002933	0.001467	0.000104	14.14	0.000
Immersio	0.000600	0.000300	0.000104	2.89	0.011
BTA*KEX	0.000633	0.000317	0.000104	3.05	0.008
BTA*Immersio	0.000367	0.000183	0.000104	1.77	0.096
KEX*Immersio	0.000250	0.000125	0.000104	1.20	0.246
BTA*KEX*Immersio	0.000350	0.000175	0.000104	1.69	0.111

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00005439	0.00005439	0.00001813	70.18	0.000
2-Way Interactions	3	0.00000359	0.00000359	0.00000120	4.63	0.016
3-Way Interactions	1	0.00000074	0.00000074	0.00000074	2.85	0.111
Residual Error	16	0.00000413	0.00000413	0.00000026		
Pure Error	16	0.00000413	0.00000413	0.00000026		
Total	23	0.00006285				

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
8	0.007200	0.008300	0.000293	-0.001100	-2.65R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007200	0.000112	64.18	0.000
BTA	-0.000300	-0.000150	0.000112	-1.34	0.200
KEX	0.002367	0.001183	0.000112	10.55	0.000
Immersio	0.000517	0.000258	0.000112	2.30	0.035
BTA*KEX	0.000767	0.000383	0.000112	3.42	0.004
BTA*Immersio	0.000450	0.000225	0.000112	2.01	0.062
KEX*Immersio	-0.000050	-0.000025	0.000112	-0.22	0.826
BTA*KEX*Immersio	0.000317	0.000158	0.000112	1.41	0.177

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003575	0.00003575	0.00001192	39.45	0.000
2-Way Interactions	3	0.00000476	0.00000476	0.00000159	5.25	0.010
3-Way Interactions	1	0.00000060	0.00000060	0.00000060	1.99	0.177
Residual Error	16	0.00000483	0.00000483	0.00000030		
Pure Error	16	0.00000483	0.00000483	0.00000030		
Total	23	0.00004594				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
8	0.007100	0.008000	0.000317	-0.000900	-2.01R
18	0.009100	0.008000	0.000317	0.001100	2.45R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007942	0.000101	78.67	0.000
BTA	-0.000350	-0.000175	0.000101	-1.73	0.102
KEX	0.002200	0.001100	0.000101	10.90	0.000
Immersio	0.000283	0.000142	0.000101	1.40	0.180
BTA*KEX	0.000900	0.000450	0.000101	4.46	0.000
BTA*Immersio	0.000483	0.000242	0.000101	2.39	0.029
KEX*Immersio	-0.000233	-0.000117	0.000101	-1.16	0.265
BTA*KEX*Immersio	0.000100	0.000050	0.000101	0.50	0.627

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003026	0.00003026	0.00001009	41.24	0.000
2-Way Interactions	3	0.00000659	0.00000659	0.00000220	8.98	0.001
3-Way Interactions	1	0.00000006	0.00000006	0.00000006	0.25	0.627
Residual Error	16	0.00000391	0.00000391	0.00000024		
Pure Error	16	0.00000391	0.00000391	0.00000024		
Total	23	0.00004082				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid

18	0.009600	0.008500	0.000286	0.001100	2.72R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008783	0.000109	80.90	0.000
BTA	0.000017	0.000008	0.000109	0.08	0.940
KEX	0.001650	0.000825	0.000109	7.60	0.000
Immersio	0.000483	0.000242	0.000109	2.23	0.041
BTA*KEX	0.000800	0.000400	0.000109	3.68	0.002
BTA*Immersio	0.000433	0.000217	0.000109	2.00	0.063
KEX*Immersio	-0.000567	-0.000283	0.000109	-2.61	0.019
BTA*KEX*Immersio	0.000150	0.000075	0.000109	0.69	0.500

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001774	0.00001774	0.00000591	20.90	0.000
2-Way Interactions	3	0.00000689	0.00000689	0.00000230	8.12	0.002
3-Way Interactions	1	0.00000014	0.00000014	0.00000014	0.48	0.500
Residual Error	16	0.00000453	0.00000453	0.00000028		
Pure Error	16	0.00000453	0.00000453	0.00000028		
Total	23	0.00002929				

Unusual Observations for 504h

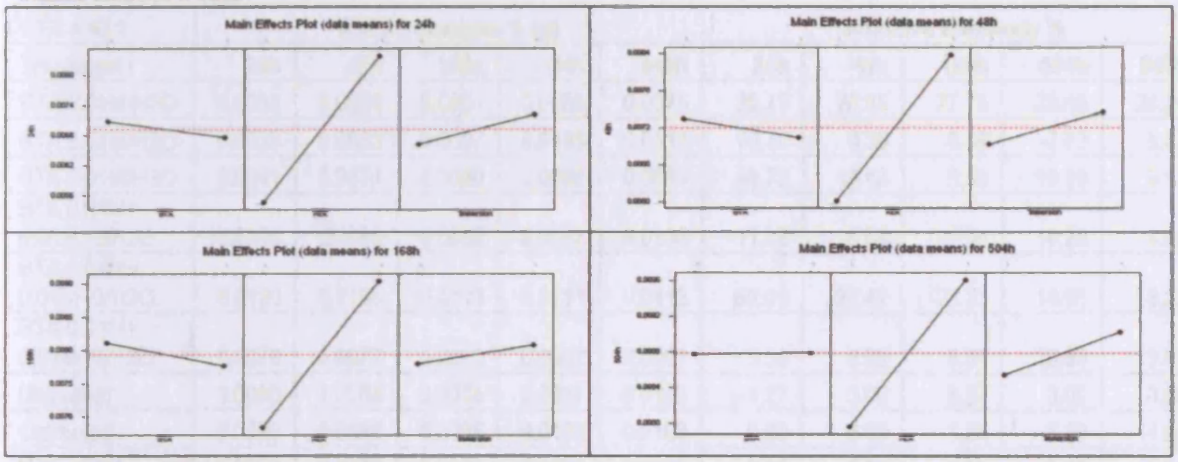
Obs	504h	Fit	StDev Fit	Residual	St Resid
18	0.010200	0.008867	0.000307	0.001333	3.07R

R denotes an observation with a large standardized residual

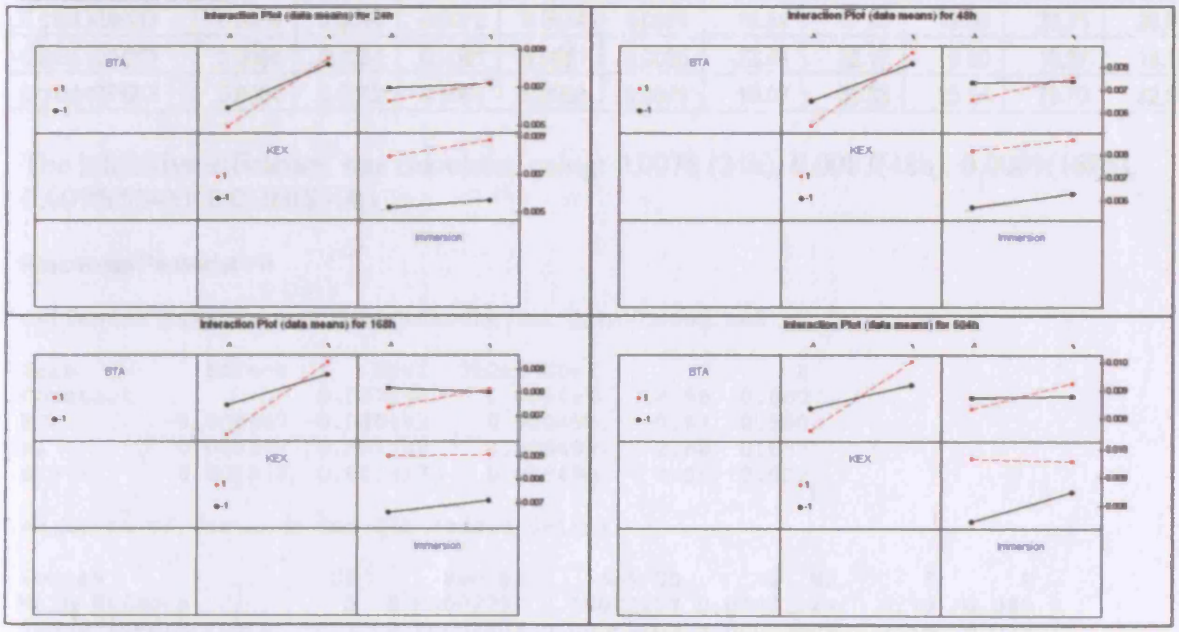
Alias Structure

-
BTA
KEX
Immersion
BTA*KEX
BTA*Immersion
KEX*Immersion
BTA*KEX*Immersion

Main Effect Plots



Interaction Plots



BTA + KI 1	Weight changes % (g)					Inhibitive Efficiency %				
Treatment	24h	48h	168h	504h	840h	24h	48h	168h	504h	840h
BTA 0.01M/H2O	0.0058	0.0059	0.0064	0.0068	0.0075	26.73	28.55	27.75	29.60	28.24
BTA 0.01M/H2O	0.0023	0.0083	0.0097	0.0105	0.0113	70.70	0.30	-8.56	-7.82	-8.57
BTA 0.01M/H2O	0.0041	0.0071	0.0080	0.0086	0.0094	48.72	14.43	9.59	10.89	9.83
BTA 0.01M+ 0.01M KI/H2O	0.0088	0.0089	0.0093	0.0097	0.0100	-11.02	-6.64	-3.94	0.20	4.08
BTA 0.01M+ 0.01M KI/H2O	0.0120	0.0106	0.0119	0.0111	0.0113	-52.03	-27.42	-33.73	-14.05	-8.26
BTA 0.01M+ 0.01M KI/H2O	0.0076	0.0077	0.0082	0.0087	0.0091	3.59	6.92	8.34	10.63	12.51
Untreated	0.0080	0.0083	0.0086	0.0097	0.0103	-1.27	0.00	3.37	0.00	0.96
Untreated	0.0079	0.0088	0.0095	0.0103	0.0109	0.00	-6.02	-6.74	-6.19	-4.81
Untreated	0.0077	0.0079	0.0087	0.0092	0.0099	2.53	4.82	2.25	5.15	4.81
0.01M KI/H2O	0.0066	0.0068	0.0072	0.0074	0.0076	16.54	17.70	19.00	23.75	26.91
0.01M KI/H2O	0.0098	0.0065	0.0081	0.0081	0.0085	-23.44	22.17	9.50	16.37	18.18
0.01M KI/H2O	0.0064	0.0062	0.0066	0.0068	0.0071	19.07	25.33	25.94	29.70	32.09

The inhibitive efficiency was calculated using: 0.0078 (24h), 0.0083(48h), 0.0089(168h), 0.0095(504h), 0.0103(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007250	0.000498	14.56	0.000
BTA	-0.000967	-0.000483	0.000498	-0.97	0.360
KI	0.002567	0.001283	0.000498	2.58	0.033
BTA*KI	0.002833	0.001417	0.000498	2.85	0.022

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00002257	0.00002257	0.00001128	3.79	0.069
2-Way Interactions	1	0.00002408	0.00002408	0.00002408	8.10	0.022
Residual Error	8	0.00002380	0.00002380	0.00000298		
Pure Error	8	0.00002380	0.00002380	0.00000298		
Total	11	0.00007045				

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007750	0.000283	27.34	0.000
BTA	0.000667	0.000333	0.000283	1.18	0.273
KI	0.000067	0.000033	0.000283	0.12	0.909
BTA*KI	0.001900	0.000950	0.000283	3.35	0.010

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000135	0.00000135	0.00000067	0.70	0.525
2-Way Interactions	1	0.00001083	0.00001083	0.00001083	11.23	0.010
Residual Error	8	0.00000771	0.00000771	0.00000096		
Pure Error	8	0.00000771	0.00000771	0.00000096		

Total	11	0.00001989	

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008517	0.000386	22.07	0.000
BTA	0.000800	0.000400	0.000386	1.04	0.330
KI	0.000067	0.000033	0.000386	0.09	0.933
BTA*KI	0.001700	0.000850	0.000386	2.20	0.059

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000193	0.00000193	0.00000097	0.54	0.602
2-Way Interactions	1	0.00000867	0.00000867	0.00000867	4.85	0.059
Residual Error	8	0.00001429	0.00001429	0.00000179		
Pure Error	8	0.00001429	0.00001429	0.00000179		
Total	11	0.00002490				

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008908	0.000342	26.07	0.000
BTA	0.000650	0.000325	0.000342	0.95	0.369
KI	-0.000550	-0.000275	0.000342	-0.80	0.444
BTA*KI	0.001750	0.000875	0.000342	2.56	0.034

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000218	0.00000218	0.00000109	0.78	0.492
2-Way Interactions	1	0.00000919	0.00000919	0.00000919	6.56	0.034
Residual Error	8	0.00001121	0.00001121	0.00000140		
Pure Error	8	0.00001121	0.00001121	0.00000140		
Total	11	0.00002257				

Estimated Effects and Coefficients for 840h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.009408	0.000341	27.57	0.000
BTA	0.000717	0.000358	0.000341	1.05	0.324
KI	-0.000950	-0.000475	0.000341	-1.39	0.201
BTA*KI	0.001683	0.000842	0.000341	2.47	0.039

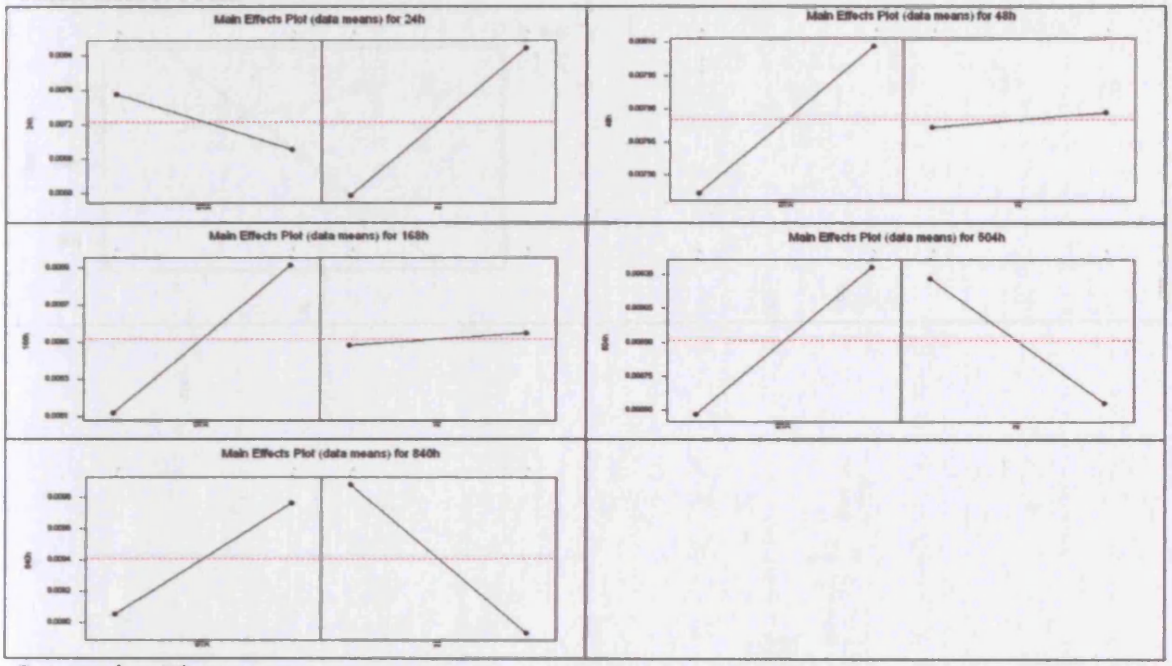
Analysis of Variance for 840h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	2	0.00000425	0.00000425	0.00000212	1.52	0.276
2-Way Interactions	1	0.00000850	0.00000850	0.00000850	6.08	0.039
Residual Error	8	0.00001118	0.00001118	0.00000140		
Pure Error	8	0.00001118	0.00001118	0.00000140		
Total	11	0.00002393				

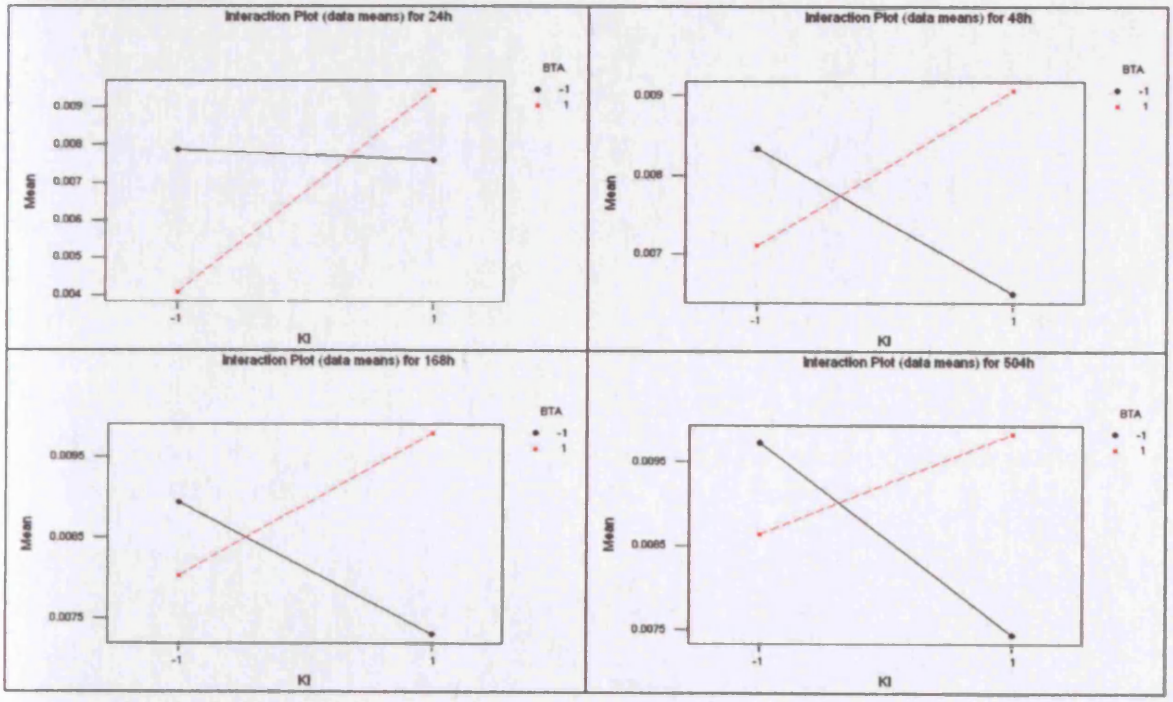
Alias Structure

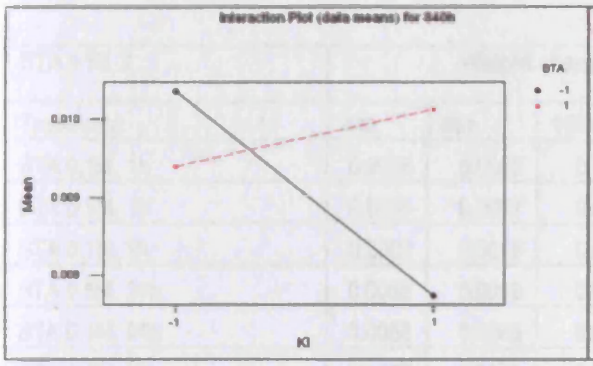
-
BTA
KI
BTA*KI

Main Effect Plots



Interaction Plots




Interaction Plot (data means) for 340h
BTA
-1
1
0.010
0.009
0.008
Mean
-1
1
KI

BTA + KI 2	Weight change %				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M, 1h	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M, 1h	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M, 1h	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M, 24h	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M, 24h	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M, 24h	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M + KI 0.1M, 1h	0.0090	0.0091	0.0097	0.0097	-18.7	-15.5	-15.5	-8.1
BTA 0.1M + KI 0.1M, 1h	0.0094	0.0096	0.0100	0.0101	-24.3	-21.0	-19.1	-12.5
BTA 0.1M + KI 0.1M, 1h	0.0099	0.0099	0.0102	0.0104	-30.8	-25.6	-20.9	-15.1
BTA 0.1M + KI 0.1M, 24h	0.0085	0.0085	0.0089	0.0090	-11.3	-7.0	-5.7	0.4
BTA 0.1M + KI 0.1M, 24h	0.0092	0.0092	0.0095	0.0097	-20.9	-16.3	-13.7	-7.5
BTA 0.1M + KI 0.1M, 24h	0.0090	0.0090	0.0092	0.0094	-18.3	-14.3	-10.1	-4.2
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.007	42.1	39.2	34.5	22.2
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M + KI 0.1M, 1h	0.0094	0.0094	0.0101	0.0092	-23.7	-19.0	-20.2	-2.8
BTA 0.25M + KI 0.1M, 1h	0.0090	0.0088	0.0089	0.0093	-18.4	-11.7	-5.8	-3.1
BTA 0.25M + KI 0.1M, 1h	0.0083	0.0090	0.0097	0.0000	-9.8	-14.5	-15.0	100.0
BTA 0.25M + KI 0.1M, 24h	0.0084	0.0089	0.0091	0.0092	-10.8	-12.2	-8.6	-2.1
BTA 0.25M + KI 0.1M, 24h	0.0093	0.0094	0.0091	0.0095	-22.5	-18.8	-8.6	-6.1
BTA 0.25M + KI 0.1M, 24h	0.0088	0.0092	0.0092	0.0093	-15.4	-15.9	-9.8	-3.1

The inhibitive efficiency was calculated using the following values of control, untreated coupons: 0.0076 (24h), 0.0079 (48h), 0.0084 (168h), 0.0090 (504h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007237	0.000087	83.19	0.000
BTA	-0.000625	-0.000313	0.000087	-3.59	0.002
KI	0.003558	0.001779	0.000087	20.45	0.000
immersio	0.000025	0.000013	0.000087	0.14	0.888
BTA*KI	0.000325	0.000162	0.000087	1.87	0.080
BTA*immersio	0.000125	0.000062	0.000087	0.72	0.483
KI*immersio	-0.000325	-0.000163	0.000087	-1.87	0.080
BTA*KI*immersio	0.000108	0.000054	0.000087	0.62	0.542

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00007832	0.00007832	0.00002611	143.70	0.000
2-Way Interactions	3	0.00000136	0.00000136	0.00000045	2.50	0.097
3-Way Interactions	1	0.00000007	0.00000007	0.00000007	0.39	0.542
Residual Error	16	0.00000291	0.00000291	0.00000018		
Pure Error	16	0.00000291	0.00000291	0.00000018		
Total	23	0.00008266				

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007592	0.000084	90.09	0.000
BTA	-0.000583	-0.000292	0.000084	-3.46	0.003
KI	0.003150	0.001575	0.000084	18.69	0.000
immersio	0.000150	0.000075	0.000084	0.89	0.387
BTA*KI	0.000483	0.000242	0.000084	2.87	0.011
BTA*immersio	0.000250	0.000125	0.000084	1.48	0.157
KI*immersio	-0.000417	-0.000208	0.000084	-2.47	0.025
BTA*KI*immersio	0.000117	0.000058	0.000084	0.69	0.499

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00006171	0.00006171	0.00002057	120.71	0.000
2-Way Interactions	3	0.00000282	0.00000282	0.00000094	5.51	0.009
3-Way Interactions	1	0.00000008	0.00000008	0.00000008	0.48	0.499
Residual Error	16	0.00000273	0.00000273	0.00000017		
Pure Error	16	0.00000273	0.00000273	0.00000017		
Total	23	0.00006734				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
21	0.005100	0.005833	0.000238	-0.000733	-2.18R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008154	0.000074	109.74	0.000
BTA	-0.000742	-0.000371	0.000074	-4.99	0.000
KI	0.002625	0.001312	0.000074	17.66	0.000
immersio	-0.000042	-0.000021	0.000074	-0.28	0.783
BTA*KI	0.000508	0.000254	0.000074	3.42	0.004
BTA*immersio	0.000275	0.000137	0.000074	1.85	0.083
KI*immersio	-0.000558	-0.000279	0.000074	-3.76	0.002
BTA*KI*immersio	-0.000108	-0.000054	0.000074	-0.73	0.477

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00004465	0.00004465	0.00001488	112.34	0.000
2-Way Interactions	3	0.00000387	0.00000387	0.00000129	9.75	0.001
3-Way Interactions	1	0.00000007	0.00000007	0.00000007	0.53	0.477
Residual Error	16	0.00000212	0.00000212	0.00000013		
Pure Error	16	0.00000212	0.00000212	0.00000013		
Total	23	0.00005072				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid

7	0.008900	0.009567	0.000210	-0.000667	-2.24R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008346	0.000390	21.41	0.000
BTA	-0.001375	-0.000687	0.000390	-1.76	0.097
KI	0.000775	0.000388	0.000390	0.99	0.335
immersio	0.001142	0.000571	0.000390	1.46	0.162
BTA*KI	-0.000592	-0.000296	0.000390	-0.76	0.459
BTA*immersio	0.001108	0.000554	0.000390	1.42	0.174
KI*immersio	0.000092	0.000046	0.000390	0.12	0.908
BTA*KI*immersio	0.000825	0.000412	0.000390	1.06	0.306

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00002277	0.00002277	0.00000759	2.08	0.143
2-Way Interactions	3	0.00000952	0.00000952	0.00000317	0.87	0.477
3-Way Interactions	1	0.00000408	0.00000408	0.00000408	1.12	0.306
Residual Error	16	0.00005835	0.00005835	0.00000365		
Pure Error	16	0.00005835	0.00005835	0.00000365		
Total	23	0.00009472				

Unusual Observations for 504h

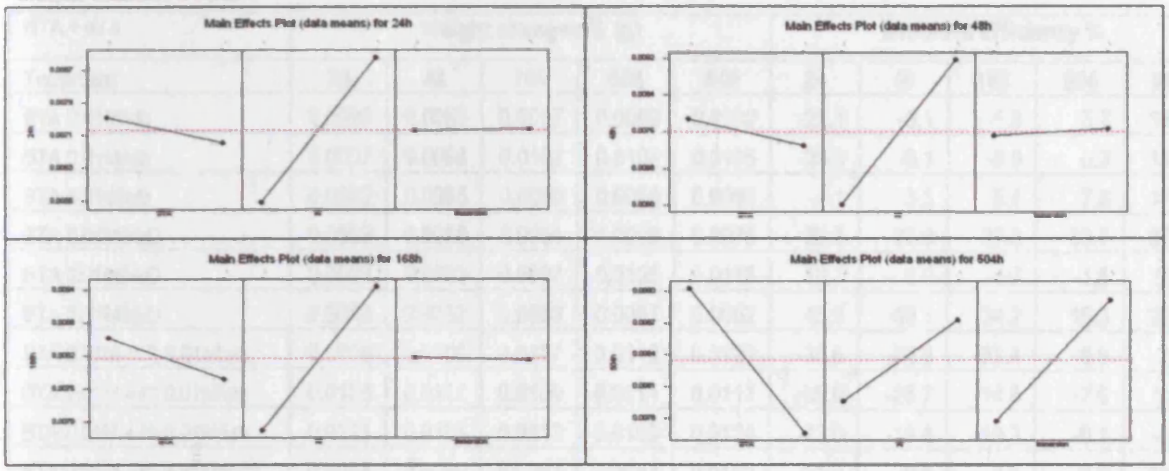
Obs	504h	Fit	StDev Fit	Residual	St Resid
7	0.009300	0.006167	0.001103	0.003133	2.01R
16	0.000000	0.006167	0.001103	-0.006167	-3.96R

R denotes an observation with a large standardized residual

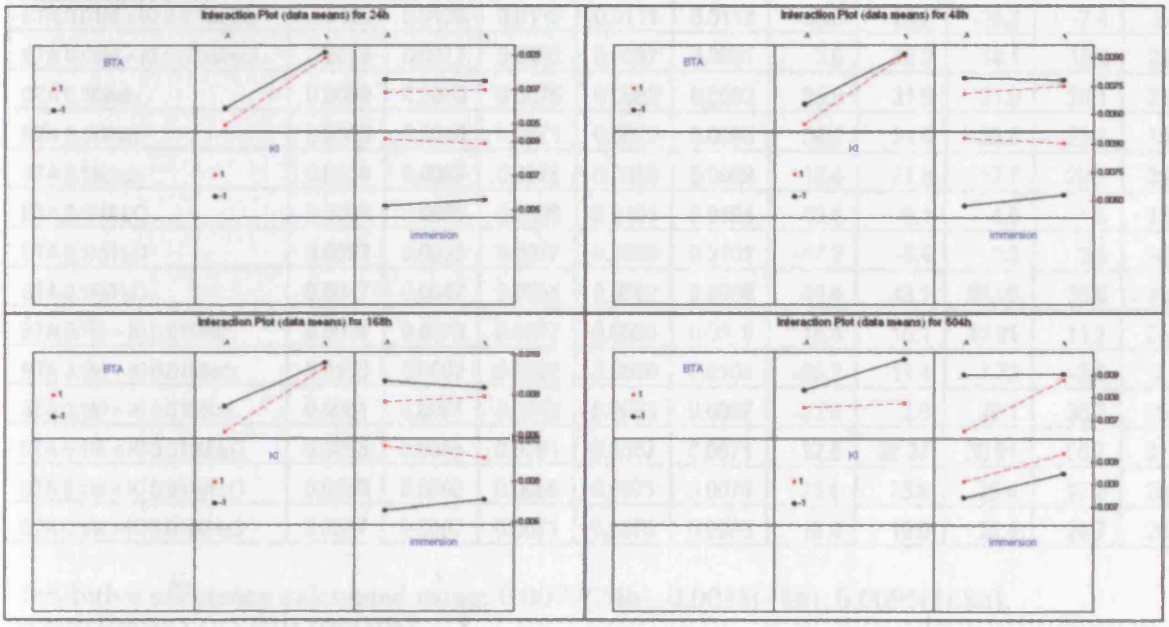
Alias Structure

I
BTA
KI
immersion
BTA*KI
BTA*immersion
KI*immersion
BTA*KI*immersion

Main Effect Plots



Interaction Plots



BTA + KI 3	Weight changes % (g)					Inhibitive Efficiency %				
Treatment	24	48	168	504	840	24	48	168	504	840
BTA 0.01M/eth	0.0096	0.0093	0.0097	0.0099	0.0102	-22.1	-6.1	-1.9	3.7	14.5
BTA 0.01M/eth	0.0097	0.0096	0.0102	0.0103	0.0105	-23.0	-9.1	-6.9	0.3	11.4
BTA 0.01M/eth	0.0082	0.0085	0.0090	0.0098	0.0098	-4.1	3.3	5.4	7.8	17.7
BTA 0.01M/H_2O	0.0058	0.0059	0.0064	0.0068	0.0075	26.7	32.6	32.3	33.7	37.3
BTA 0.01M/H_2O	0.0023	0.0083	0.0097	0.0105	0.0113	70.7	6.0	-1.7	-1.5	5.1
BTA 0.01M/H_2O	0.0043	0.0053	0.0063	0.0087	0.0092	45.3	40.1	34.2	15.3	22.7
BTA 0.01M + KI 0.01M/eth	0.0108	0.0109	0.0127	0.0112	0.0122	-36.6	-23.8	-33.4	-8.8	-2.5
BTA 0.01M + KI 0.01M/eth	0.0126	0.0111	0.0109	0.0111	0.0117	-59.9	-25.7	-14.8	-7.6	1.8
BTA 0.01M + KI 0.01M/eth	0.0113	0.0105	0.0113	0.0109	0.0124	-43.0	-19.4	-19.3	-6.1	-4.3
BTA 0.01M + KI 0.01M/H_2O	0.0088	0.0089	0.0093	0.0097	0.0100	-11.0	-0.6	2.6	6.0	16.2
BTA 0.01M + KI 0.01M/H_2O	0.0120	0.0106	0.0119	0.0111	0.0113	-52.0	-20.2	-25.3	-7.4	5.4
BTA 0.01M + KI 0.01M/H_2O	0.0076	0.0077	0.0082	0.0087	0.0091	3.6	12.2	14.1	15.8	23.5
BTA 0.1M/eth	0.0059	0.0060	0.0075	0.0082	0.0093	25.9	31.9	21.0	20.1	21.5
BTA 0.1M/eth	0.0055	0.0060	0.0071	0.0079	0.0096	30.2	31.8	25.0	23.4	19.0
BTA 0.1M/eth	0.0064	0.0069	0.0078	0.0080	0.0089	18.4	21.8	17.7	22.1	25.5
BTA 0.1M/H_2O	0.0094	0.0096	0.0099	0.0101	0.0104	-19.4	-9.1	-4.0	1.6	13.0
BTA 0.1M/H_2O	0.0093	0.0093	0.0097	0.0099	0.0101	-17.2	-5.4	-2.3	3.6	14.9
BTA 0.1M/H_2O	0.0047	0.0047	0.0055	0.0062	0.0069	40.4	43.1	38.08	35.6	33.9
BTA 0.1M + KI 0.01M/eth	0.0064	0.0070	0.0077	0.0086	0.0079	18.4	16.1	13.01	11.7	24.1
BTA 0.1M + KI 0.01M/eth	0.0100	0.0092	0.0096	0.0099	0.0104	-26.2	-11.4	-7.73	-2.6	0.1
BTA 0.1M + KI 0.01M/eth	0.0081	0.0081	0.0063	0.0063	0.0067	-3.06	2.9	29.1	35.2	35.5
BTA 0.1M + KI 0.01M/H_2O	0.0053	0.0055	0.0061	0.0067	0.0071	32.6	33.37	30.91	30.7	31.3
BTA 0.1M + KI 0.01M/H_2O	0.0060	0.0062	0.0066	0.0071	0.0074	23.6	25.8	25.4	27.2	28.7
BTA 0.1M + KI 0.01M/H_2O	0.0067	0.0067	0.0071	0.0073	0.0076	15.4	19.0	20.4	24.7	26.5

Inhibitive efficiency calculated using: 0.0079(24h), 0.0088(48h), 0.0095(168h), 0.0103(504h) and 0.0119(840h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007758	0.000330	23.51	0.000
BTA	-0.001650	-0.000825	0.000330	-2.50	0.024
KI	0.002083	0.001042	0.000330	3.16	0.006
Solvent	0.001817	0.000908	0.000330	2.75	0.014
BTA*KI	-0.001783	-0.000892	0.000330	-2.70	0.016
BTA*Solvent	-0.001750	-0.000875	0.000330	-2.65	0.017
KI*Solvent	0.000317	0.000158	0.000330	0.48	0.638
BTA*KI*Solvent	0.001783	0.000892	0.000330	2.70	0.016

Analysis of Variance for 24 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P

Main Effects	3	0.00006218	0.00006218	0.00002073	7.93	0.002
2-Way Interactions	3	0.00003806	0.00003806	0.00001269	4.85	0.014
3-Way Interactions	1	0.00001908	0.00001908	0.00001908	7.30	0.016
Residual Error	16	0.00004182	0.00004182	0.00000261		
Pure Error	16	0.00004182	0.00004182	0.00000261		
Total	23	0.00016114				

Unusual Observations for 24

Obs	24	Fit	StDev Fit	Residual	St Resid
19	0.004700	0.007800	0.000933	-0.003100	-2.35R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007996	0.000274	29.18	0.000
BTA	-0.001775	-0.000888	0.000274	-3.24	0.005
KI	0.001075	0.000537	0.000274	1.96	0.067
Solvent	0.001208	0.000604	0.000274	2.20	0.042
BTA*KI	-0.001058	-0.000529	0.000274	-1.93	0.071
BTA*Solvent	-0.000992	-0.000496	0.000274	-1.81	0.089
KI*Solvent	0.000658	0.000329	0.000274	1.20	0.247
BTA*KI*Solvent	0.001092	0.000546	0.000274	1.99	0.064

Analysis of Variance for 48 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003460	0.00003460	0.00001153	6.40	0.005
2-Way Interactions	3	0.00001522	0.00001522	0.00000507	2.81	0.073
3-Way Interactions	1	0.00000715	0.00000715	0.00000715	3.97	0.064
Residual Error	16	0.00002884	0.00002884	0.00000180		
Pure Error	16	0.00002884	0.00002884	0.00000180		
Total	23	0.00008581				

Unusual Observations for 48

Obs	48	Fit	StDev Fit	Residual	St Resid
19	0.004700	0.007867	0.000775	-0.003167	-2.89R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168 (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008596	0.000305	28.15	0.000
BTA	-0.002075	-0.001038	0.000305	-3.40	0.004
KI	0.000758	0.000379	0.000305	1.24	0.232
Solvent	0.001075	0.000537	0.000305	1.76	0.098
BTA*KI	-0.001408	-0.000704	0.000305	-2.31	0.035
BTA*Solvent	-0.000925	-0.000463	0.000305	-1.51	0.149
KI*Solvent	0.000475	0.000238	0.000305	0.78	0.448
BTA*KI*Solvent	0.000642	0.000321	0.000305	1.05	0.309

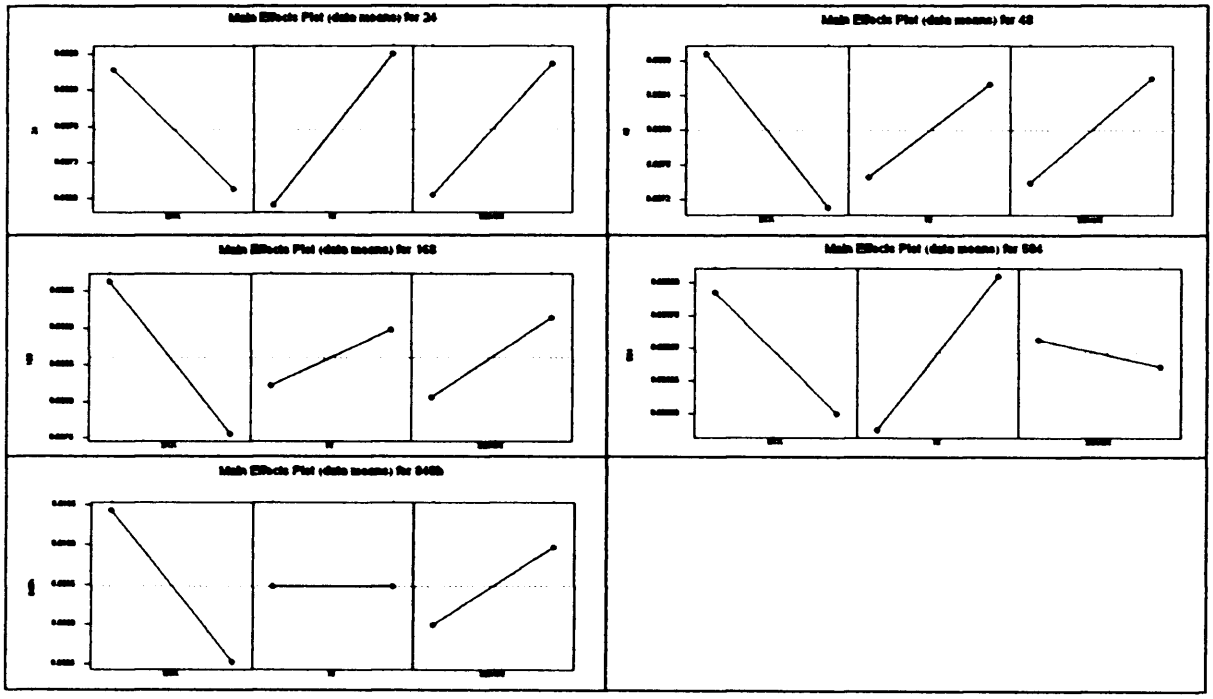
Analysis of Variance for 168 (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00003622	0.00003622	0.00001207	5.39	0.009
2-Way Interactions	3	0.00001839	0.00001839	0.00000613	2.74	0.078
3-Way Interactions	1	0.00000247	0.00000247	0.00000247	1.10	0.309
Residual Error	16	0.00003581	0.00003581	0.00000224		
Pure Error	16	0.00003581	0.00003581	0.00000224		

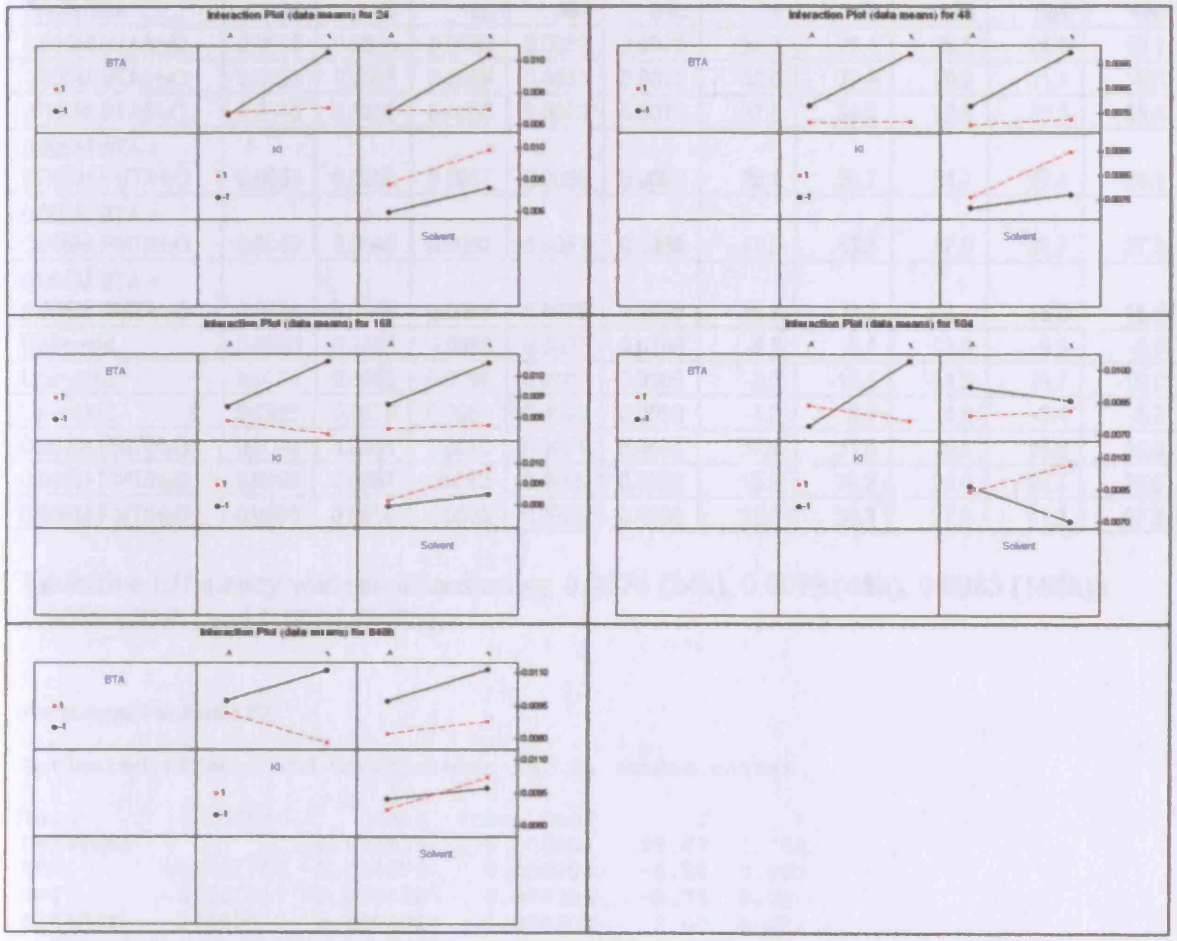
```
Total                 23  0.00009289

Unusual Observations for 168

Obs        168        Fit  StDev Fit   Residual   St Resid
 19   0.005500   0.008367   0.000864  -0.002867      -2.35R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504 (coded units)

Term               Effect      Coef  StDev Coef       T      P
Constant                    0.008462    0.000561   15.09  0.000
BTA             -0.000925 -0.000462    0.000561   -0.82  0.422
KI               0.001175  0.000587    0.000561    1.05  0.310
Solvent         -0.000208 -0.000104    0.000561   -0.19  0.855
BTA*KI          -0.001875 -0.000937    0.000561   -1.67  0.114
BTA*Solvent      0.000442  0.000221    0.000561    0.39  0.699
KI*Solvent       0.001442  0.000721    0.000561    1.29  0.217
BTA*KI*Solvent  -0.000442 -0.000221    0.000561   -0.39  0.699

Analysis of Variance for 504 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           3  0.00001368  0.00001368  0.00000456   0.60  0.622
2-Way Interactions     3  0.00003473  0.00003473  0.00001158   1.53  0.244
3-Way Interactions     1  0.00000117  0.00000117  0.00000117   0.16  0.699
Residual Error        16  0.00012077  0.00012077  0.00000755
  Pure Error          16  0.00012077  0.00012077  0.00000755
Total                 23  0.00017036

Unusual Observations for 504

Obs        504        Fit  StDev Fit   Residual   St Resid
 22  -0.001800   0.006133   0.001586  -0.007933      -3.54R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term               Effect      Coef  StDev Coef       T      P
Constant                    0.009479    0.000256   36.98  0.000
BTA             -0.001908 -0.000954    0.000256   -3.72  0.002
KI               0.000008  0.000004    0.000256    0.02  0.987
Solvent          0.000975  0.000487    0.000256    1.90  0.075
BTA*KI          -0.001358 -0.000679    0.000256   -2.65  0.017
BTA*Solvent     -0.000425 -0.000212    0.000256   -0.83  0.419
KI*Solvent       0.000492  0.000246    0.000256    0.96  0.352
BTA*KI*Solvent  -0.000075 -0.000038    0.000256   -0.15  0.886

Analysis of Variance for 840 (coded units)

Source                DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects           3  0.00002755  0.00002755  0.00000918   5.83  0.007
2-Way Interactions     3  0.00001360  0.00001360  0.00000453   2.88  0.069
3-Way Interactions     1  0.00000003  0.00000003  0.00000003   0.02  0.886
Residual Error        16  0.00002523  0.00002523  0.00000158
  Pure Error          16  0.00002523  0.00002523  0.00000158
Total                 23  0.00006642

Unusual Observations for 840

Obs        840        Fit  StDev Fit   Residual   St Resid
```

```
 12    0.010400    0.008333    0.000725    0.002067        2.02R
 19    0.006900    0.009133    0.000725   -0.002233       -2.18R

R denotes an observation with a large standardized residual

Alias Structure

-
BTA
KI
Solvent
BTA*KI
BTA*Solvent
KI*Solvent
BTA*KI*Solvent
```

Main Effect Plots



Interaction Plots



BTA and PMT 1	Weight Changes % (g)					Inhibitive Efficiency %				
Treatment	24	48	168	504	840	24	48	168	504	840
0.005M BTA/H_2O	0.0058	0.0058	0.0059	0.0068	0.0076	23.7	26.4	28.5	24.0	19.1
0.005M BTA/H_2O	0.0053	0.0055	0.0059	0.0061	0.0077	30.0	29.8	29.2	31.1	18.5
0.005M BTA/H_2O	0.0048	0.0052	0.0056	0.0063	0.0070	37.0	34.6	32.8	29.5	25.4
0.005M BTA + 0.005M PMT/H_2O	0.0054	0.0058	0.0057	0.0065	0.0069	28.4	26.7	31.7	27.4	26.1
0.005M BTA + 0.005M PMT/H_2O	0.0040	0.0045	0.0052	0.0061	0.0068	47.9	43.6	37.9	31.7	27.9
0.005M BTA + 0.005M PMT/H_2O	0.0056	0.0061	0.0068	0.0075	0.0080	26.4	22.8	18.1	15.5	15.0
Untreated	0.0080	0.0083	0.0086	0.0097	0.0103	-5.3	-5.1	-3.6	-9.0	-9.6
Untreated	0.0079	0.0088	0.0095	0.0103	0.0109	-3.9	-11.4	-14.5	-15.7	-16.0
Untreated	0.0077	0.0079	0.0087	0.0092	0.0099	-1.3	0.0	-4.8	-3.4	-5.3
0.005M PMT/H_2O	0.0048	0.0054	0.0070	0.0074	0.0080	37.4	31.8	15.8	16.5	15.0
0.005M PMT/H_2O	0.0064	0.0057	0.0063	0.0066	0.0072	15.9	28.2	24.0	25.7	23.5
0.005M PMT/H_2O	0.0066	0.0050	0.0052	0.0026	0.0030	12.6	36.3	37.6	71.3	67.8

Inhibitive Efficiency was calculated using: 0.0076 (24h), 0.0079 (48h), 0.0083 (168h), 0.0089 (504h) and 0.0094 (840h).

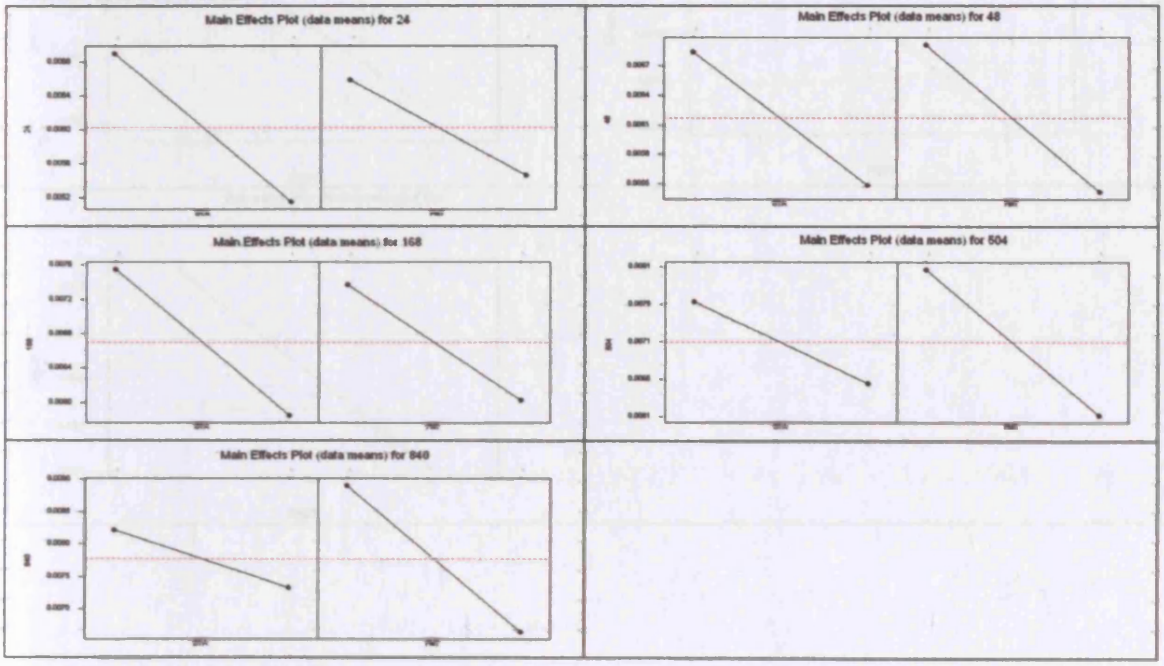
Fractional Factorial Fit

```
Estimated Effects and Coefficients for 24 (coded units)

Term          Effect      Coef  StDev Coef       T      P
Constant                0.006025    0.000204   29.47  0.000
BTA       -0.001750 -0.000875    0.000204   -4.28  0.003
PMT       -0.001117 -0.000558    0.000204   -2.73  0.026
BTA*PMT    0.000817  0.000408    0.000204    2.00  0.081

Analysis of Variance for 24 (coded units)

Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00001293  0.00001293  0.00000646  12.89  0.003
2-Way Interactions    1  0.00000200  0.00000200  0.00000200   3.99  0.081
Residual Error        8  0.00000401  0.00000401  0.00000050
  Pure Error          8  0.00000401  0.00000401  0.00000050
Total                11  0.00001894

Estimated Effects and Coefficients for 48 (coded units)

Term          Effect      Coef  StDev Coef       T      P
Constant                0.006167    0.000154   40.01  0.000
BTA       -0.001367 -0.000683    0.000154   -4.43  0.002
PMT       -0.001500 -0.000750    0.000154   -4.87  0.001
BTA*PMT    0.001467  0.000733    0.000154    4.76  0.001

Analysis of Variance for 48 (coded units)

Source               DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects          2  0.00001235  0.00001235  0.00000618  21.67  0.001
2-Way Interactions    1  0.00000645  0.00000645  0.00000645  22.64  0.001
```

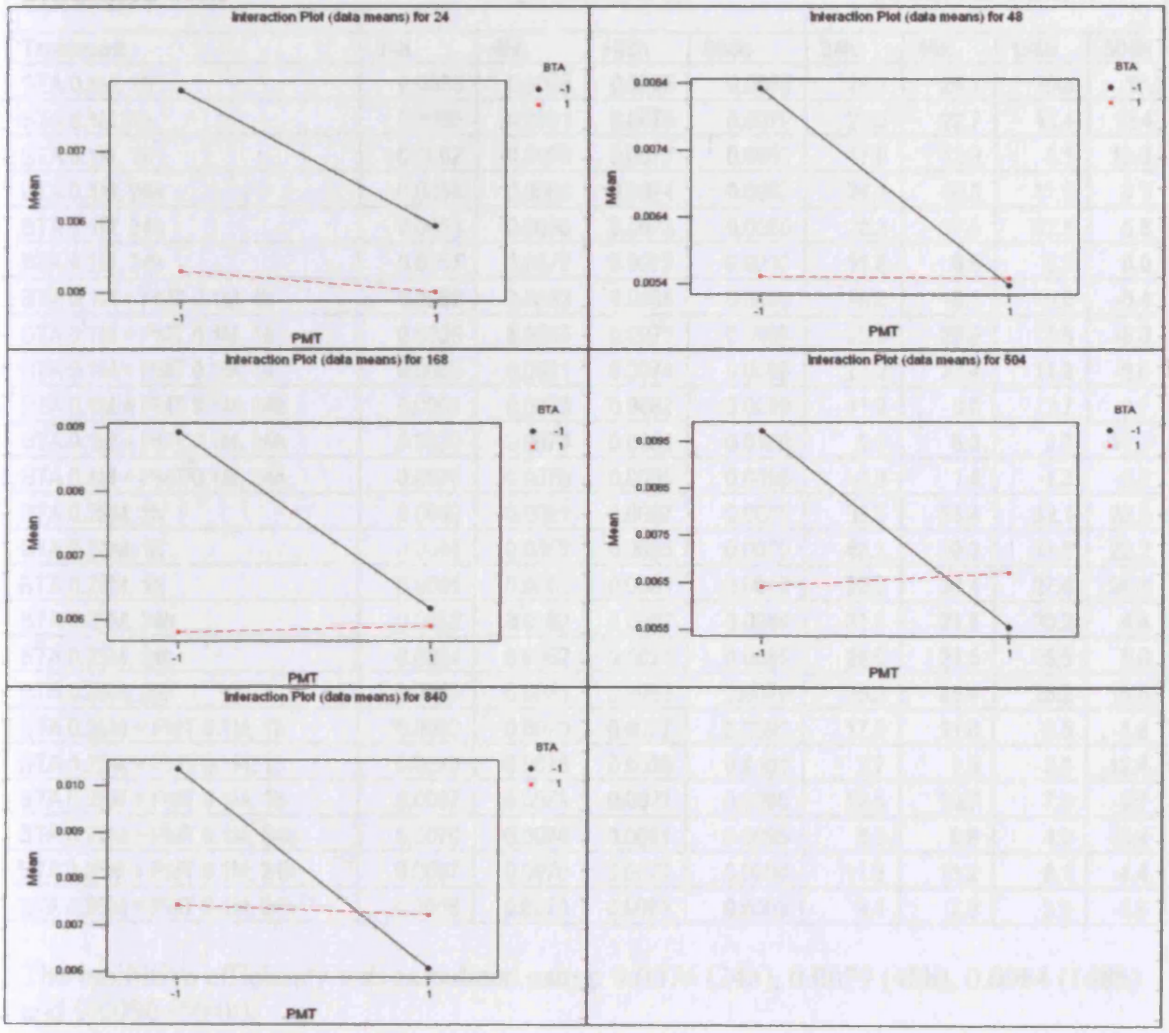
```
Residual Error          8  0.00000228 0.00000228 0.00000029
  Pure Error            8  0.00000228 0.00000228 0.00000028
Total                  11  0.00002109

Unusual Observations for 48

Obs         48        Fit  StDev Fit   Residual   St Resid
  7   0.004500   0.005467   0.000308  -0.000967      -2.22R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant                0.006700    0.000192   34.92  0.000
BTA       -0.001700 -0.000850    0.000192   -4.43  0.002
PMT       -0.001333 -0.000667    0.000192   -3.47  0.008
BTA*PMT    0.001433  0.000717    0.000192    3.74  0.006

Analysis of Variance for 168 (coded units)

Source                 DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects            2  0.00001400  0.00001400  0.00000700  15.85  0.002
2-Way Interactions      1  0.00000616  0.00000616  0.00000616  13.95  0.006
Residual Error          8  0.00000353  0.00000353  0.00000044
  Pure Error            8  0.00000353  0.00000353  0.00000044
Total                  11  0.00002370

Estimated Effects and Coefficients for 504 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant                0.007092    0.000397   17.86  0.000
BTA       -0.001083 -0.000542    0.000397   -1.36  0.210
PMT       -0.001950 -0.000975    0.000397   -2.46  0.040
BTA*PMT    0.002250  0.001125    0.000397    2.83  0.022

Analysis of Variance for 504 (coded units)

Source                 DF      Seq SS      Adj SS      Adj MS      F      P
Main Effects            2  0.00001493  0.00001493  0.00000746   3.95  0.064
2-Way Interactions      1  0.00001519  0.00001519  0.00001519   8.03  0.022
Residual Error          8  0.00001513  0.00001513  0.00000189
  Pure Error            8  0.00001513  0.00001513  0.00000189
Total                  11  0.00004525

Unusual Observations for 504

Obs        504        Fit  StDev Fit   Residual   St Resid
 10   0.002600   0.005533   0.000794  -0.002933      -2.61R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 840 (coded units)

Term         Effect      Coef  StDev Coef       T      P
Constant                0.007775    0.000410   18.98  0.000
BTA       -0.000883 -0.000442    0.000410   -1.08  0.312
PMT       -0.002250 -0.001125    0.000410   -2.75  0.025
BTA*PMT    0.002050  0.001025    0.000410    2.50  0.037

Analysis of Variance for 840 (coded units)

Source                 DF      Seq SS      Adj SS      Adj MS      F      P
```

```
Main Effects             2  0.00001753 0.00001753 0.00000876   4.35  0.053
2-Way Interactions       1  0.00001261 0.00001261 0.00001261   6.26  0.037
Residual Error           8  0.00001611 0.00001611 0.00000201
  Pure Error             8  0.00001611 0.00001611 0.00000201
Total                   11  0.00004624

Unusual Observations for 840

Obs        840        Fit  StDev Fit   Residual   St Resid
 10   0.003000   0.006067   0.000819  -0.003067      -2.65R

R denotes an observation with a large standardized residual

Alias Structure

I
BTA
PMT
BTA*PMT
```

Main Effect Plots



Interaction Plots



BTA + PMT 2	Weight Change % (g)				Inhibitive Efficiency %			
Treatment	24h	48h	168h	504h	24h	48h	168h	504h
BTA 0.1M, 1h	0.0056	0.0060	0.0075	0.0080	26.2	24.1	10.6	10.8
BTA 0.1M, 1h	0.0055	0.0061	0.0070	0.0079	28.2	22.7	16.4	12.4
BTA 0.1M, 1h	0.0062	0.0069	0.0077	0.0080	17.8	12.9	8.1	10.8
BTA 0.1M, 24h	0.0058	0.0066	0.0074	0.0087	24.1	16.3	11.9	3.9
BTA 0.1M, 24h	0.0058	0.0065	0.0073	0.0085	23.3	17.6	12.8	5.8
BTA 0.1M, 24h	0.0067	0.0072	0.0079	0.0090	11.8	9.5	5.6	0.0
BTA 0.1M + PMT 0.1M, 1h	0.0082	0.0083	0.0088	0.0098	-8.0	-5.1	-5.0	-8.4
BTA 0.1M + PMT 0.1M, 1h	0.0056	0.0063	0.0073	0.0095	25.9	20.6	13.6	-5.8
BTA 0.1M + PMT 0.1M, 1h	0.0055	0.0061	0.0074	0.0096	27.2	23.4	11.9	-6.6
BTA 0.1M + PMT 0.1M, 24h	0.0068	0.0073	0.0082	0.0099	11.2	8.0	2.7	-9.7
BTA 0.1M + PMT 0.1M, 24h	0.0070	0.0074	0.0082	0.0100	8.3	6.0	2.3	-11.3
BTA 0.1M + PMT 0.1M, 24h	0.0076	0.0078	0.0085	0.0098	-0.5	1.4	-1.3	-8.9
BTA 0.25M, 1h	0.0049	0.0051	0.0057	0.0069	35.5	35.4	32.1	23.3
BTA 0.25M, 1h	0.0044	0.0048	0.0055	0.0070	42.1	39.2	34.5	22.2
BTA 0.25M, 1h	0.0051	0.0055	0.0061	0.0068	32.9	30.4	27.4	24.4
BTA 0.25M, 24h	0.0052	0.0062	0.0067	0.0086	31.6	21.5	20.2	4.4
BTA 0.25M, 24h	0.0054	0.0062	0.0071	0.0085	28.9	21.5	15.5	5.6
BTA 0.25M, 24h	0.0049	0.0051	0.0062	0.0076	35.5	35.4	26.2	15.6
BTA 0.25M + PMT 0.1M, 1h	0.0062	0.0070	0.0077	0.0091	17.9	11.8	8.5	-1.6
BTA 0.25M + PMT 0.1M, 1h	0.0073	0.0078	0.0086	0.0101	3.7	1.5	-2.0	-12.6
BTA 0.25M + PMT 0.1M, 1h	0.0067	0.0071	0.0077	0.0095	12.5	10.7	7.8	-5.7
BTA 0.25M + PMT 0.1M, 24h	0.0070	0.0074	0.0081	0.0095	8.5	6.3	4.0	-5.4
BTA 0.25M + PMT 0.1M, 24h	0.0067	0.0070	0.0077	0.0094	11.6	11.2	8.1	-4.4
BTA 0.25M + PMT 0.1M, 24h	0.0069	0.0073	0.0081	0.0093	9.4	7.9	3.9	-3.6

The inhibitive efficiency was calculated using: 0.0076 (24h), 0.0079 (48h), 0.0084 (168h) and 0.0090 (504h).

Fractional Factorial Fit

Estimated Effects and Coefficients for 24h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006125	0.000134	45.69	0.000
BTA	-0.000467	-0.000233	0.000134	-1.74	0.101
PMT	0.001333	0.000667	0.000134	4.97	0.000
Immersio	0.000383	0.000192	0.000134	1.43	0.172
BTA*PMT	0.000483	0.000242	0.000134	1.80	0.090
BTA*Immersio	-0.000133	-0.000067	0.000134	-0.50	0.626
PMT*Immersio	0.000033	0.000017	0.000134	0.12	0.903
BTA*PMT*Immersio	-0.000150	-0.000075	0.000134	-0.56	0.584

Analysis of Variance for 24h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001285	0.00001286	0.00000428	9.94	0.001
2-Way Interactions	3	0.00000152	0.00000152	0.00000051	1.17	0.352
3-Way Interactions	1	0.00000014	0.00000014	0.00000014	0.31	0.584

Residual Error	16	0.00000690	0.00000690	0.00000043
Pure Error	16	0.00000690	0.00000690	0.00000043
Total	23	0.00002141		

Unusual Observations for 24h

Obs	24h	Fit	StDev Fit	Residual	St Resid
2	0.008200	0.006433	0.000379	0.001767	3.29R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 48h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.006625	0.000119	55.90	0.000
BTA	-0.000500	-0.000250	0.000119	-2.11	0.051
PMT	0.001217	0.000608	0.000119	5.13	0.000
Immersio	0.000417	0.000208	0.000119	1.76	0.098
BTA*PMT	0.000567	0.000283	0.000119	2.39	0.029
BTA*Immersio	-0.000100	-0.000050	0.000119	-0.42	0.679
PMT*Immersio	-0.000150	-0.000075	0.000119	-0.63	0.536
BTA*PMT*Immersio	-0.000233	-0.000117	0.000119	-0.98	0.340

Analysis of Variance for 48h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001142	0.00001142	0.00000381	11.30	0.000
2-Way Interactions	3	0.00000212	0.00000212	0.00000071	2.10	0.141
3-Way Interactions	1	0.00000033	0.00000033	0.00000033	0.97	0.340
Residual Error	16	0.00000539	0.00000539	0.00000034		
Pure Error	16	0.00000539	0.00000539	0.00000034		
Total	23	0.00001926				

Unusual Observations for 48h

Obs	48h	Fit	StDev Fit	Residual	St Resid
2	0.008300	0.006900	0.000335	0.001400	2.95R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 168h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.007433	0.000091	81.77	0.000
BTA	-0.000667	-0.000333	0.000091	-3.67	0.002
PMT	0.001183	0.000592	0.000091	6.51	0.000
Immersio	0.000367	0.000183	0.000091	2.02	0.061
BTA*PMT	0.000583	0.000292	0.000091	3.21	0.005
BTA*Immersio	0.000067	0.000033	0.000091	0.37	0.719
PMT*Immersio	-0.000150	-0.000075	0.000091	-0.83	0.421
BTA*PMT*Immersio	-0.000317	-0.000158	0.000091	-1.74	0.101

Analysis of Variance for 168h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00001188	0.00001188	0.00000396	19.96	0.000
2-Way Interactions	3	0.00000220	0.00000220	0.00000073	3.70	0.034
3-Way Interactions	1	0.00000060	0.00000060	0.00000060	3.03	0.101
Residual Error	16	0.00000317	0.00000317	0.00000020		
Pure Error	16	0.00000317	0.00000317	0.00000020		
Total	23	0.00001785				

Unusual Observations for 168h

Obs	168h	Fit	StDev Fit	Residual	St Resid
2	0.008800	0.007833	0.000257	0.000967	2.66R

R denotes an observation with a large standardized residual

Estimated Effects and Coefficients for 504h (coded units)

Term	Effect	Coef	StDev Coef	T	P
Constant		0.008792	0.000059	148.09	0.000
BTA	-0.000533	-0.000267	0.000059	-4.49	0.000
PMT	0.001667	0.000833	0.000059	14.04	0.000
Immersio	0.000550	0.000275	0.000059	4.63	0.000
BTA*PMT	0.000250	0.000125	0.000059	2.11	0.051
BTA*Immersio	0.000033	0.000017	0.000059	0.28	0.783
PMT*Immersio	-0.000500	-0.000250	0.000059	-4.21	0.001
BTA*PMT*Immersio	-0.000250	-0.000125	0.000059	-2.11	0.051

Analysis of Variance for 504h (coded units)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main Effects	3	0.00002019	0.00002019	0.00000673	79.56	0.000
2-Way Interactions	3	0.00000188	0.00000188	0.00000063	7.42	0.002
3-Way Interactions	1	0.00000038	0.00000038	0.00000038	4.43	0.051
Residual Error	16	0.00000135	0.00000135	0.00000008		
Pure Error	16	0.00000135	0.00000135	0.00000008		
Total	23	0.00002380				

Unusual Observations for 504h

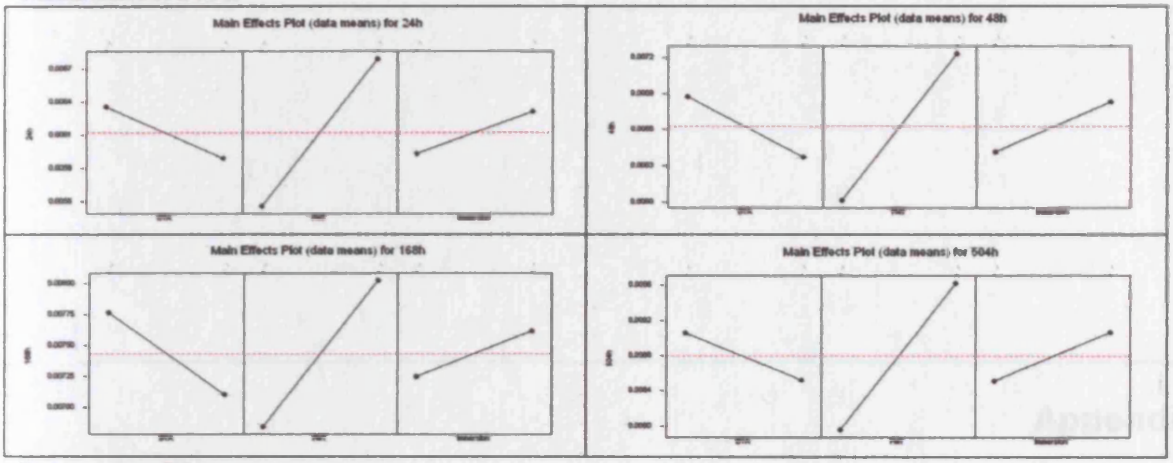
Obs	504h	Fit	StDev Fit	Residual	St Resid
11	0.010100	0.009567	0.000168	0.000533	2.25R
18	0.007600	0.008233	0.000168	-0.000633	-2.67R

R denotes an observation with a large standardized residual

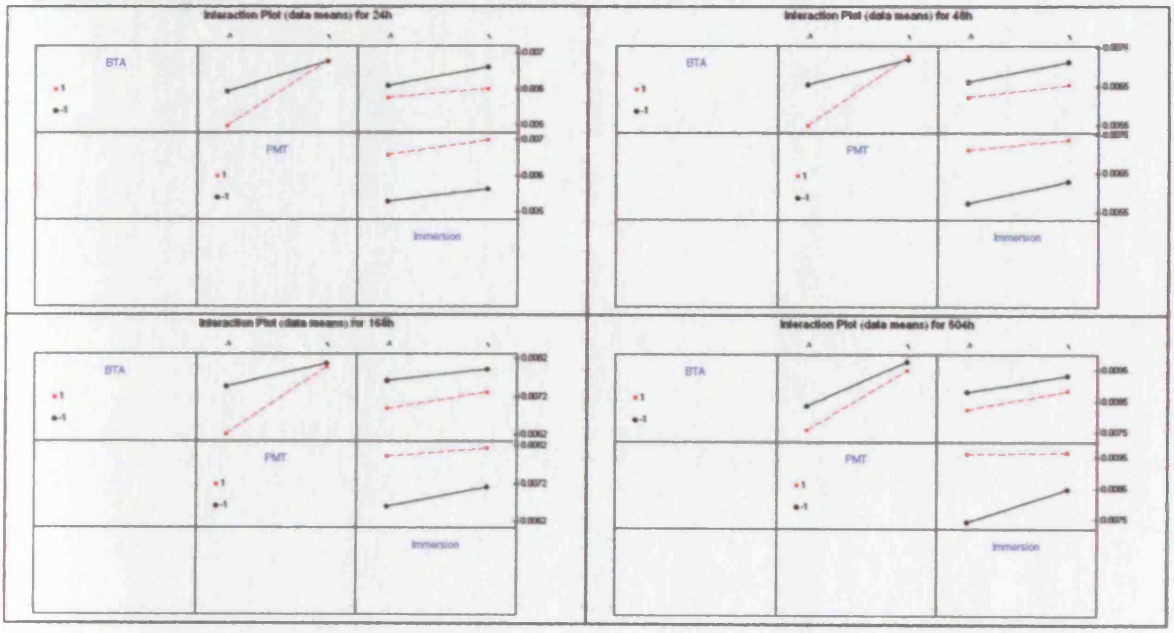
Alias Structure

I
BTA
PMT
Immersion
BTA*PMT
BTA*Immersion
PMT*Immersion
BTA*PMT*Immersion

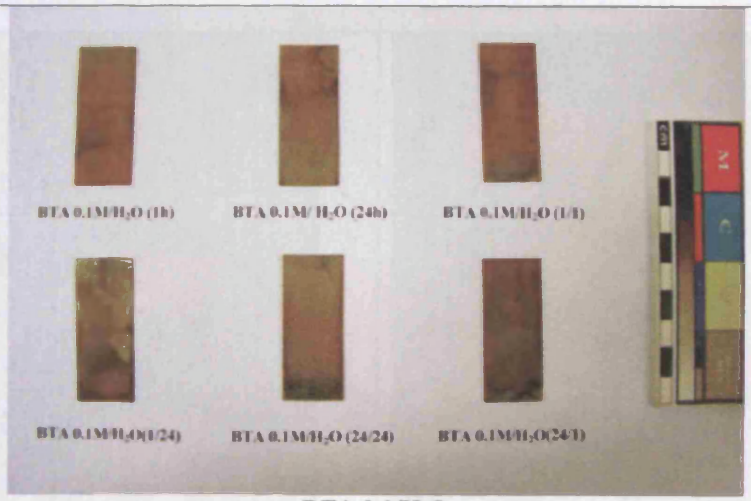
Main Effect Plots



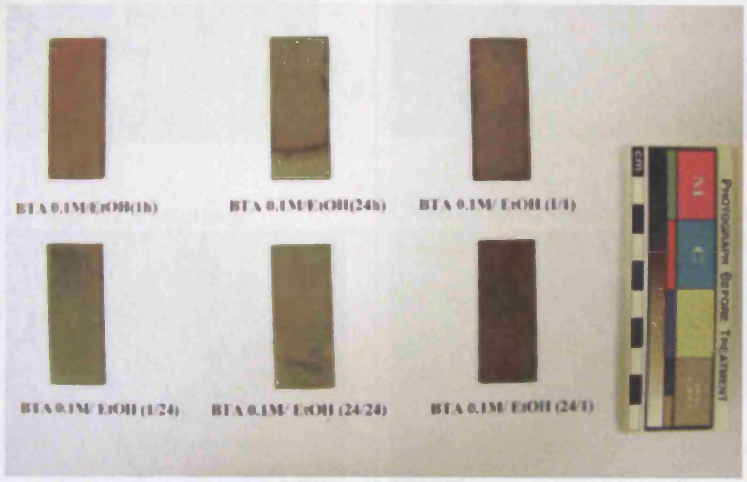
Interaction Plots



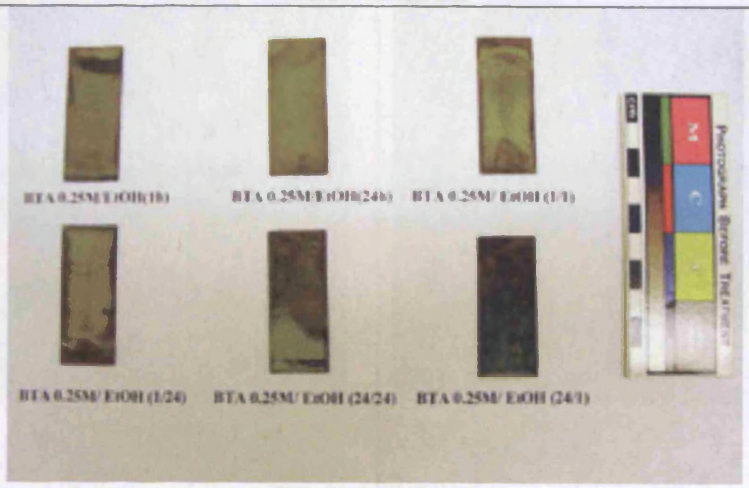
Appendix 2



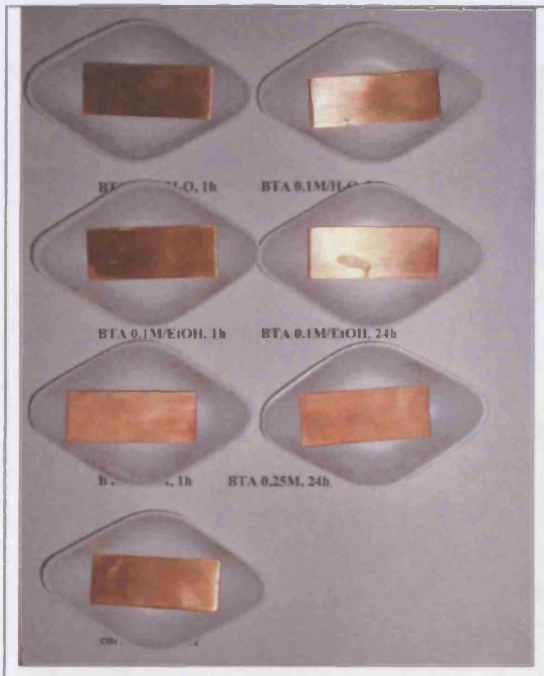
BTA 0.1/H_2O



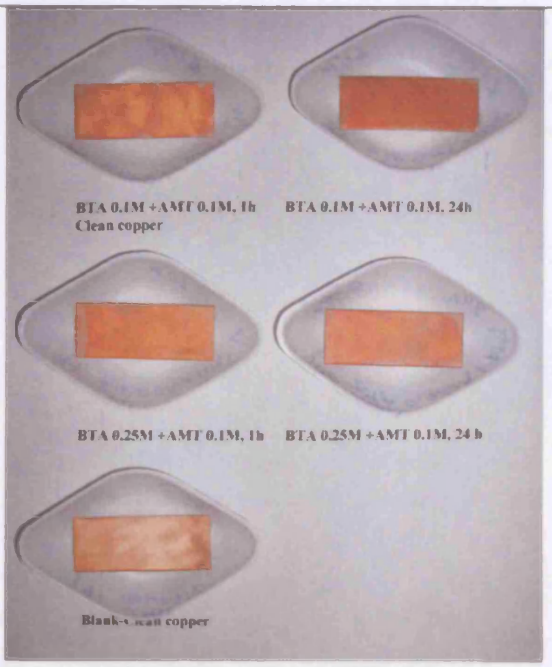
BTA 0.1M/EtOH



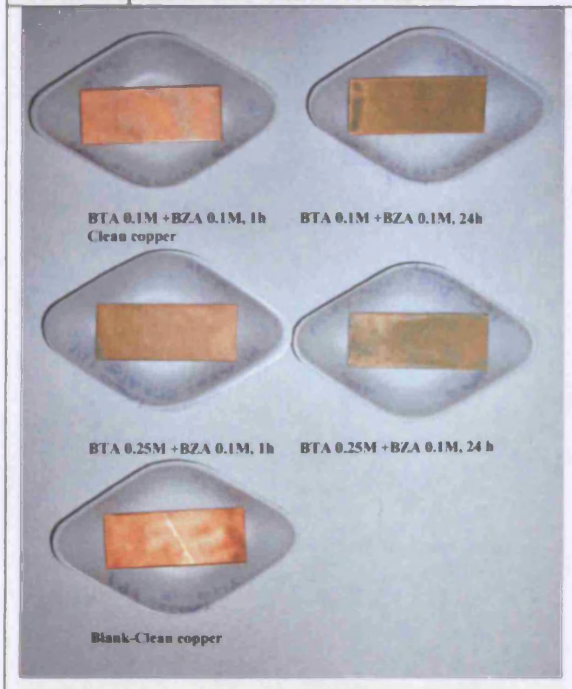
BTA 0.25M/EtOH



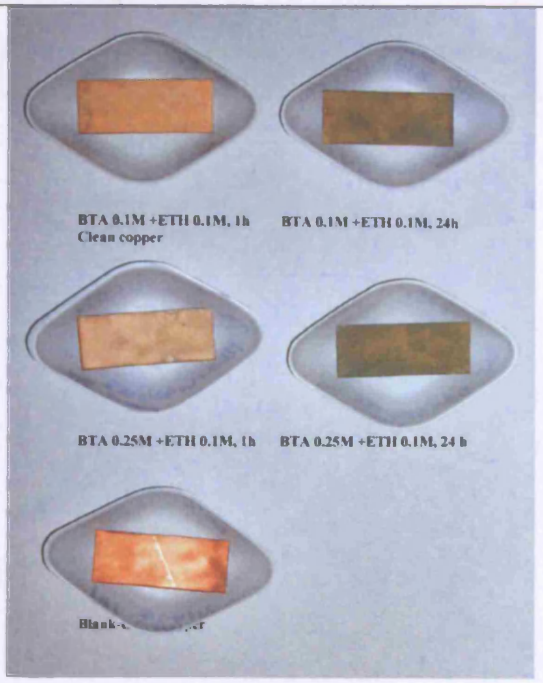
Clean coupons treated with BTA solutions



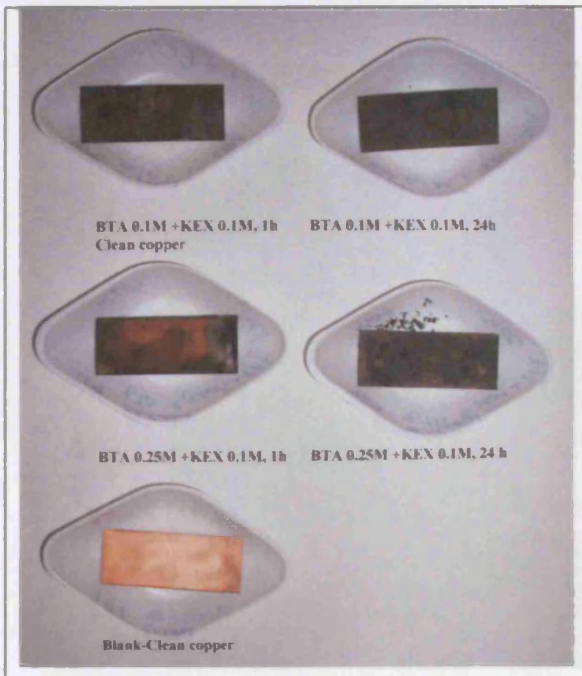
Clean coupons treated with BTA + AMT solutions



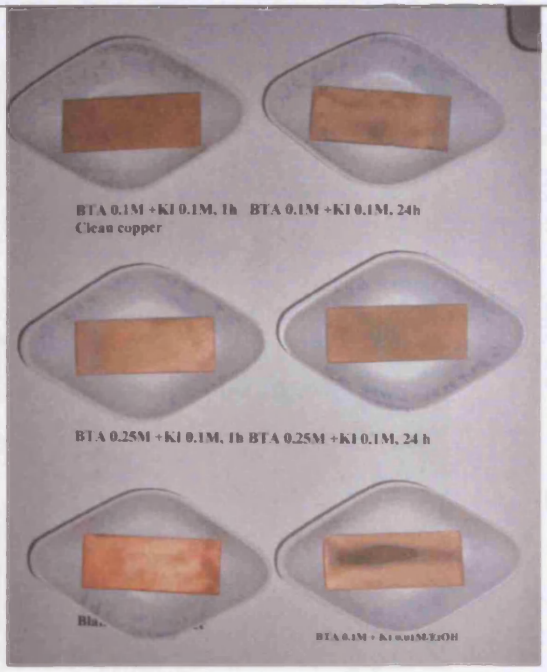
Clean coupons treated with BTA + BZA solutions



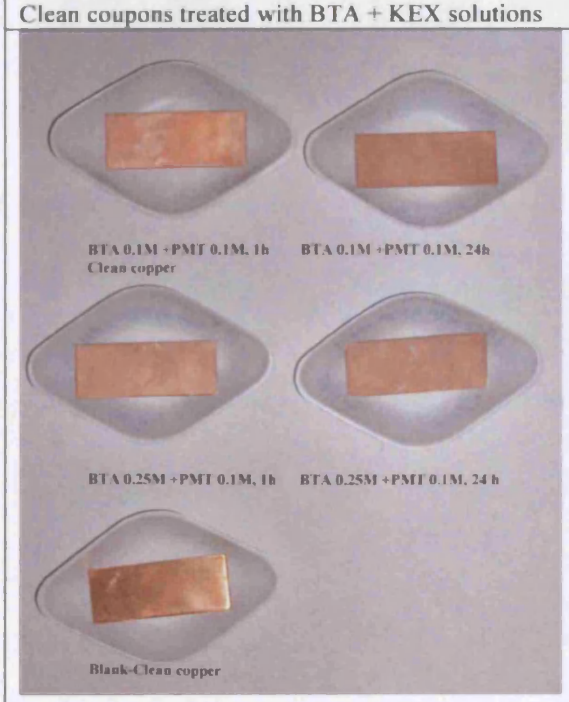
Clean coupons treated with BTA + ETH solutions



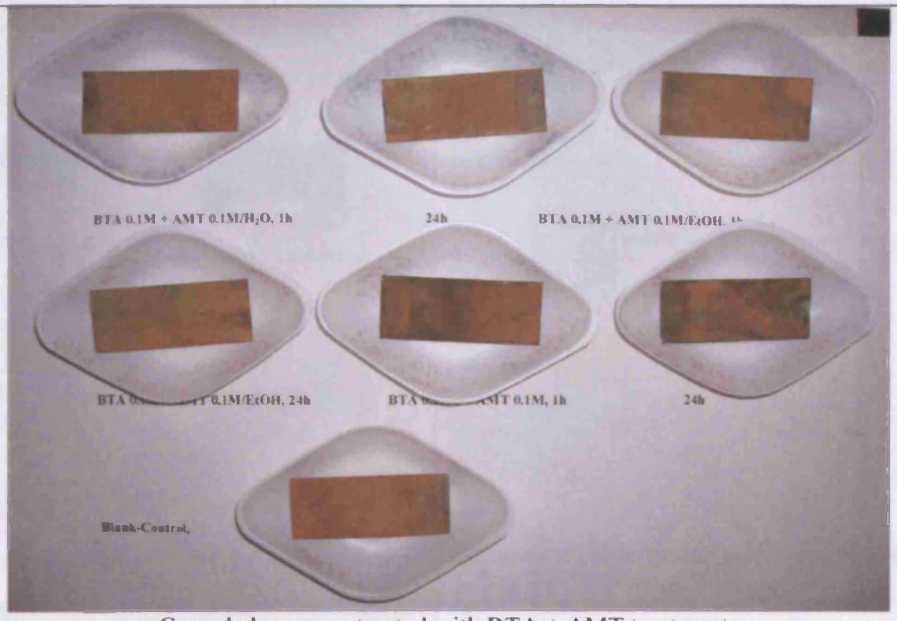
Clean coupons treated with BTA + KEX solutions



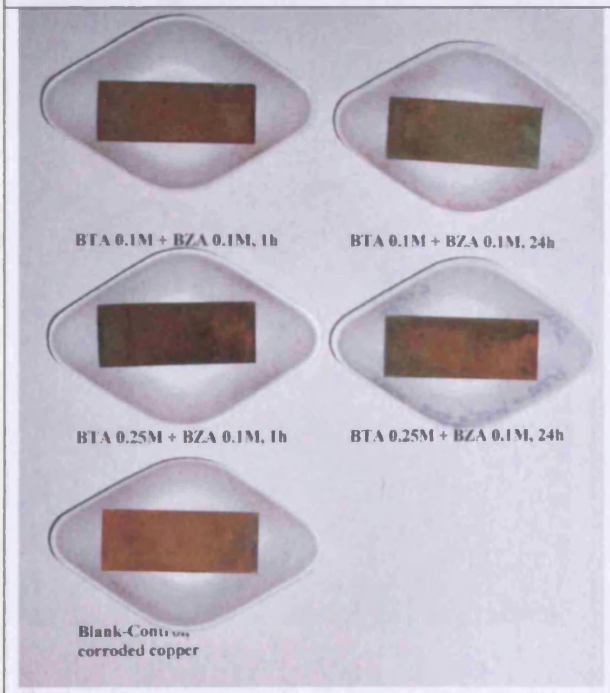
Clean coupons treated with BTA + KI solutions



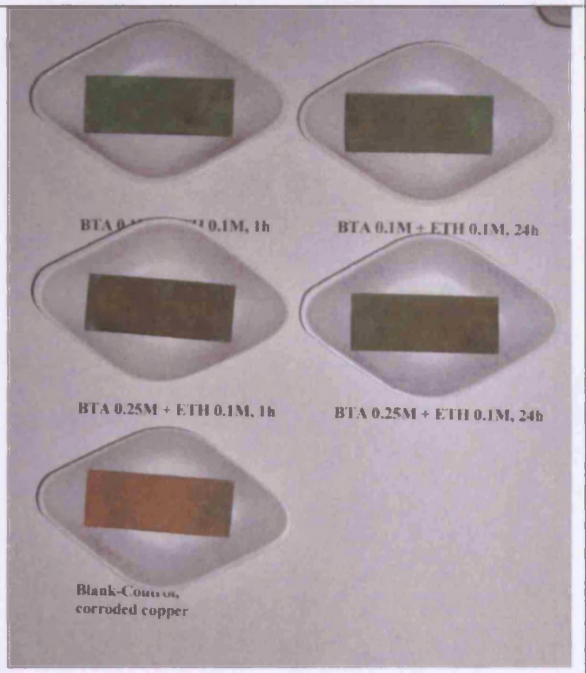
Clean coupons treated with BTA + PMT solutions



Corroded coupons treated with BTA + AMT treatments

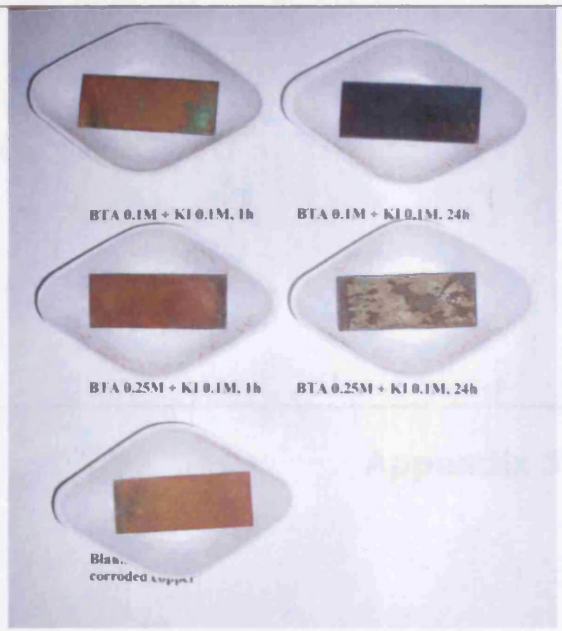


Corroded coupons treated with BTA + BZA solutions

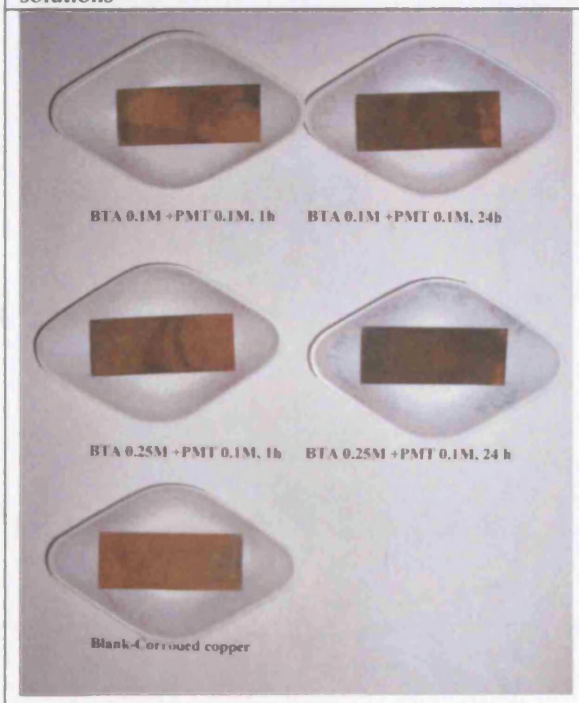


Corroded coupons treated with BTA + ETH solutions

Corroded coupons treated with BTA + KEX solutions



Corroded coupons treated with BTA + KI solutions



Corroded coupons treated with BTA + PMT solutions

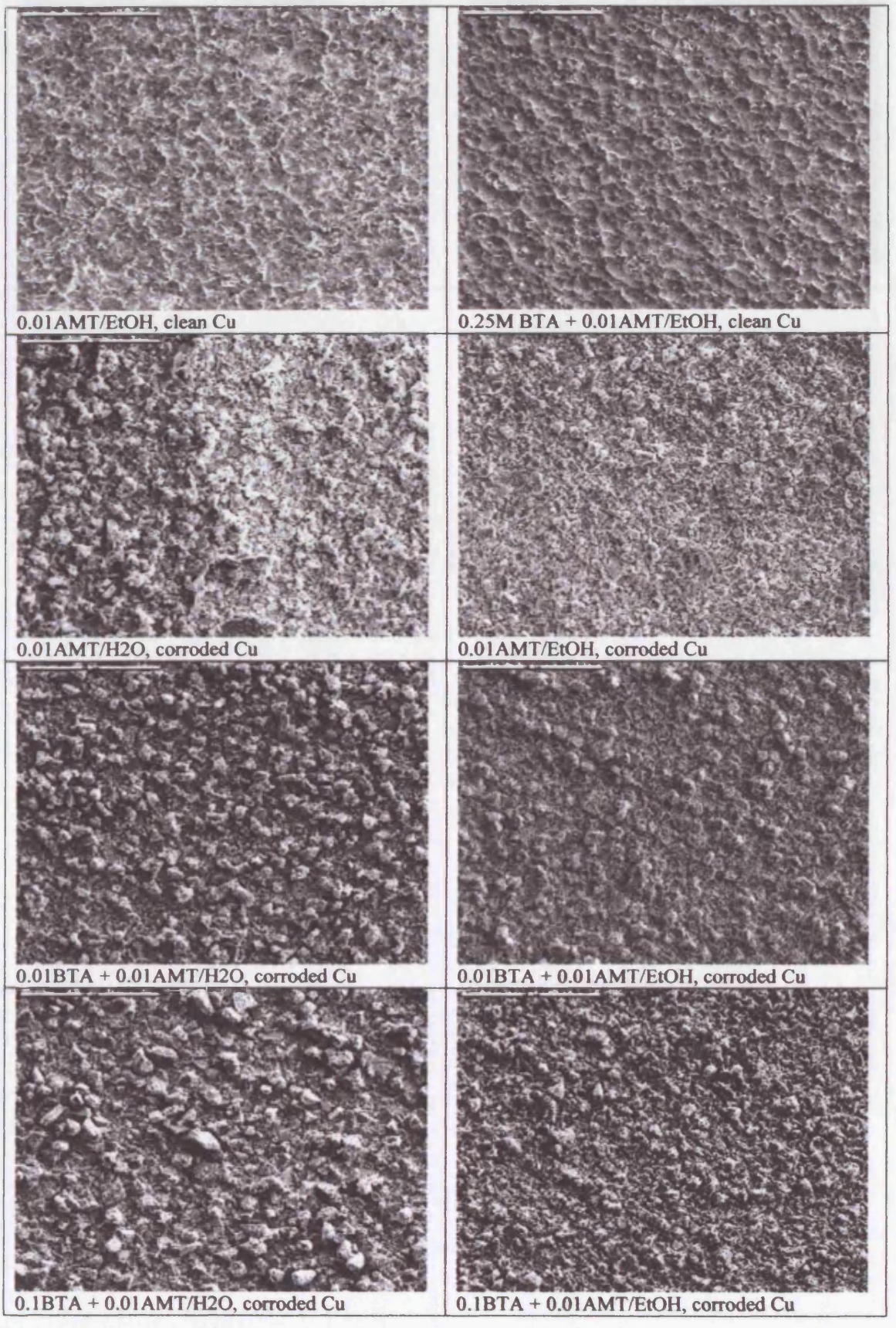
Appendix 3

Colour Measurements

Treatment	L	a	b	DL	Da	Db	DE
Corroded copper	54.36	17.69	28.69				
BTA 0.1M, H2O, 1h	44.86	12.12	23.23	-9.50	-5.57	-5.46	12.29
BTA 0.1M, H2O, 24h	45.93	5.19	22.40	-8.42	-12.51	-6.29	16.34
BTA 0.1M, H2O, 1/1h	43.27	10.37	19.35	-11.09	-7.32	-9.35	16.24
BTA 0.1M/H2O, 1/24H	44.57	6.00	20.01	-9.78	-11.70	-8.68	17.55
BTA 0.1/H2O, 24/1H	43.46	3.77	16.66	-10.90	-13.93	-12.04	21.39
BTA 0.1M/H2O, 24/24H	48.10	4.06	20.63	-6.26	-13.64	-8.06	17.03
BTA 0.1M/EtOH, 1h	43.23	5.28	15.66	-11.13	-12.41	-13.03	21.16
BTA 0.1M/EtOH, 24h	46.20	-1.39	13.65	-8.16	-19.08	-15.05	25.63
BTA 0.1M/EtOH, 1/1h	42.14	2.77	17.69	-12.22	-14.93	-11.00	22.21
BTA 0.1M/EtOH, 1/24h	44.24	-4.80	10.33	-10.12	-22.49	-18.37	30.75
BTA 0.1M/EtOH, 24/1h	35.41	5.94	20.97	-18.95	-11.75	-7.72	23.60
BTA 0.1M/EtOH, 24/24h	45.37	-3.27	9.37	-8.98	-20.96	-19.32	29.89
BTA 0.25M 1h	40.94	2.73	13.90	-13.42	-14.97	-14.79	24.96
BTA 0.25 24h	48.88	-3.26	13.98	-5.48	-20.95	-14.72	26.18
BTA 0.25 1/1h	57.36	-4.45	13.82	3.00	-22.14	-14.87	26.84
BTA 0.25 1/24h	33.95	-3.14	15.19	-20.41	-20.83	-13.50	32.13
BTA 0.25, 24/1h	57.48	-4.39	13.97	3.13	-22.08	-14.72	26.72
BTA 0.25, 24/24h	46.84	-3.94	12.84	-7.51	-21.63	-15.86	27.85
BTA 0.005M/ H2O	56.96	-1.91	25.31	2.61	-19.61	-3.38	20.06
BTA 2 ppm	47.59	6.76	22.73	-6.77	-10.93	-5.96	14.17
BTA 0.001M/ H2O	52.30	10.30	31.35	-2.06	-7.40	2.65	8.12
BTA 0.01M/H2O	48.68	11.56	23.24	-5.68	-6.14	-5.45	9.98
BTA 0.01M/ EtOH	43.37	9.69	32.87	-10.99	-8.01	4.18	14.22
PMT 0.005M/ H2O	42.28	0.51	12.79	-12.08	-17.18	-15.90	26.34
BTA 0.005 + PMT 0.005M/ H2O	54.73	-5.79	16.89	0.37	-23.48	-11.80	26.28
ETH 1.8 ppm	49.88	8.69	28.64	-4.48	-9.01	-0.06	10.06
BTA 2ppm + ETH 1.8ppm	51.56	10.05	30.04	-2.79	-7.64	1.34	8.24
BTA 2ppm + ETH 2.6 ppm	43.54	3.78	16.32	-10.82	-13.92	-12.37	21.54
KEX 0.01M	51.83	7.67	39.95	-2.53	-10.02	11.25	15.28
KEX 0.01M + BTA 0.001M	48.62	5.53	41.96	-5.74	-12.16	13.27	18.89
BTA + KEX	54.69	7.14	35.35	0.33	-10.55	6.65	12.48
0.25M BTA + 0.1M KEX	65.70	0.20	-20.39	11.35	-17.49	-49.09	53.33
KI 0.01M/H2O	61.48	6.66	19.13	7.12	-11.03	-9.56	16.24
BTA 0.01M + KI 0.01M/H2O	68.88	0.47	13.46	14.52	-17.22	-15.23	27.19
BTA 0.01M + KI 0.01M/EtOH	49.54	8.16	16.16	-4.82	-9.54	-12.53	16.47
BTA 0.01M + KI 0.01M/ EtOH	52.72	3.54	13.66	-1.64	-14.15	-15.03	20.71
BTA 0.1M + KI 0.01M/EtOH	52.28	5.94	17.91	-2.08	-11.76	-10.78	16.08
BTA 0.1M + 0.1M KI	63.59	5.92	-18.85	9.23	-11.78	-47.54	49.84
BTA 0.25 M + 0.1M KI	95.06	-1.39	-11.36	40.70	-19.09	-40.05	60.23
BTA 0.1M +AMT/eth, 1h	41.65	9.11	24.93	-12.71	-8.58	-3.76	15.79
BTA 0.1M BTA+ 0.01M AMT/eth, 24h	44.05	6.29	22.82	-10.31	-11.41	-5.88	16.46
BTA 0.1+ 0.01M AMT/w	45.60	2.51	23.77	-8.75	-15.19	-4.93	18.21
0.25M +AMT	42.01	9.24	27.27	-12.35	-8.45	-1.42	15.03

Appendix 4

SEM: BTA + AMT



0.01AMT/EtOH, clean Cu

0.25M BTA + 0.01AMT/EtOH, clean Cu

0.01AMT/H2O, corroded Cu

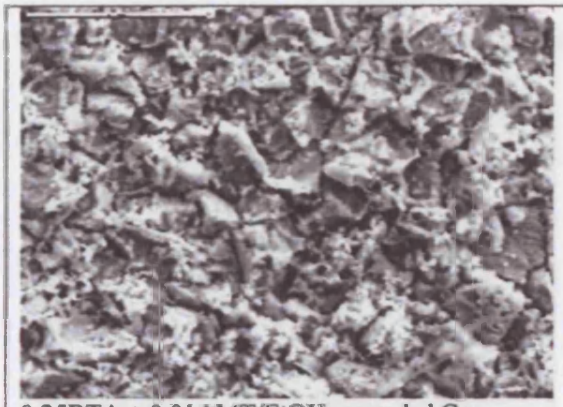
0.01AMT/EtOH, corroded Cu

0.01BTA + 0.01AMT/H2O, corroded Cu

0.01BTA + 0.01AMT/EtOH, corroded Cu

0.1BTA + 0.01AMT/H2O, corroded Cu

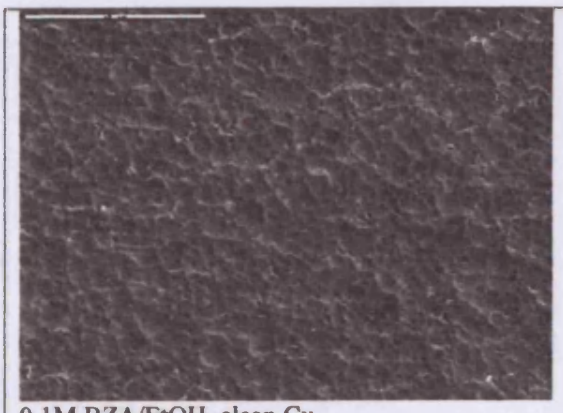
0.1BTA + 0.01AMT/EtOH, corroded Cu



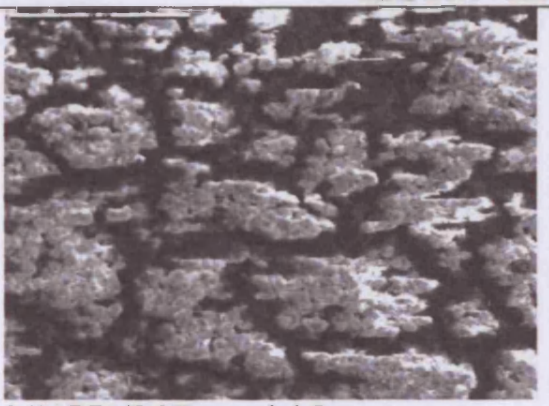
0.25BTA + 0.01AMT/EtOH, corroded Cu

0.1BTA + 0.01AMT/EtOH, corroded Cu

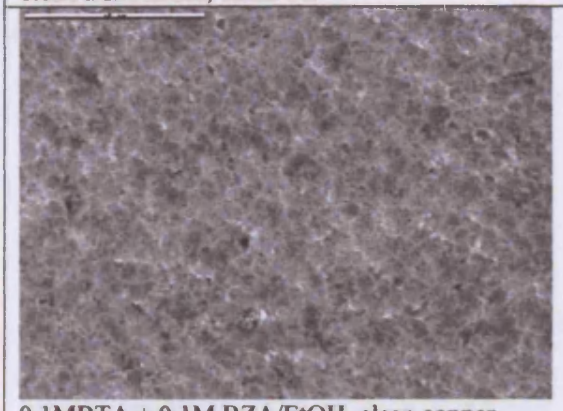
SEM: BTA + BZA



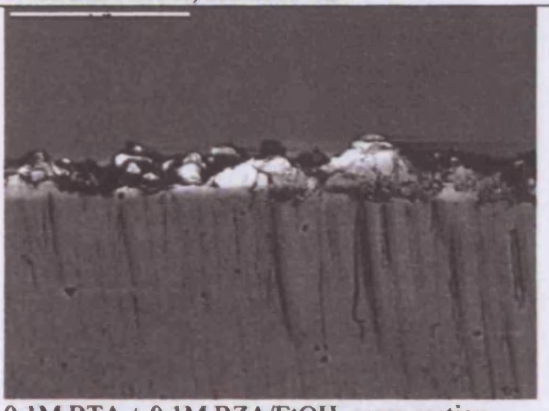
0.1M BZA/EtOH, clean Cu



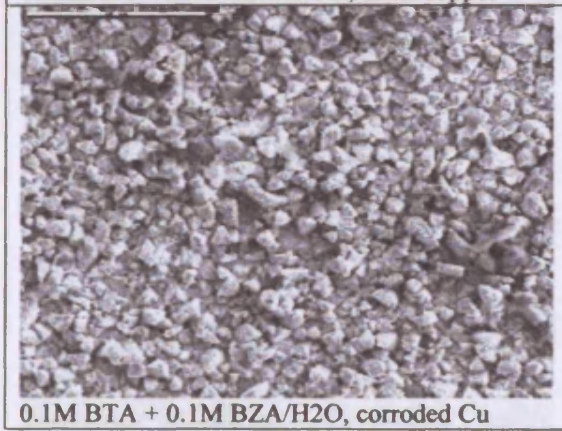
0.1M BZA/EtOH, corroded Cu



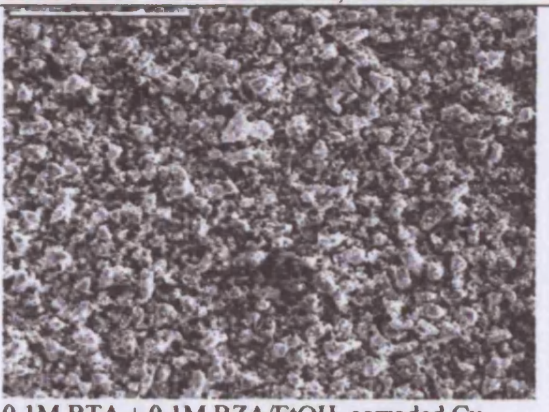
0.1MBTA + 0.1M BZA/EtOH, clean copper



0.1M BTA + 0.1M BZA/EtOH, cross section



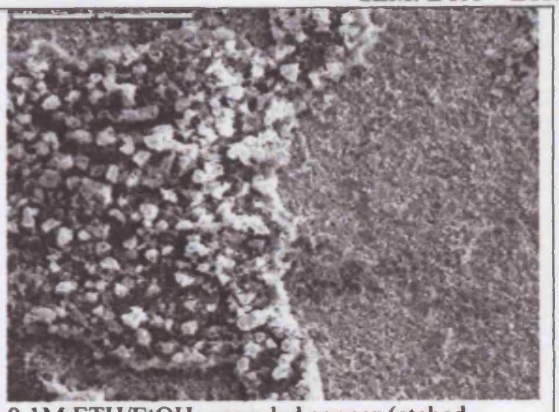
0.1M BTA + 0.1M BZA/H2O, corroded Cu



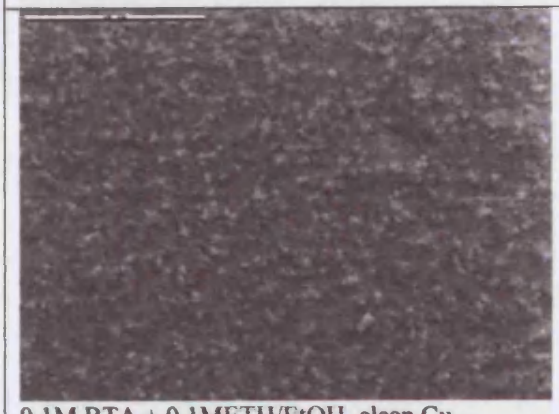
0.1M BTA + 0.1M BZA/EtOH, corroded Cu

SEM: BTA + ETH

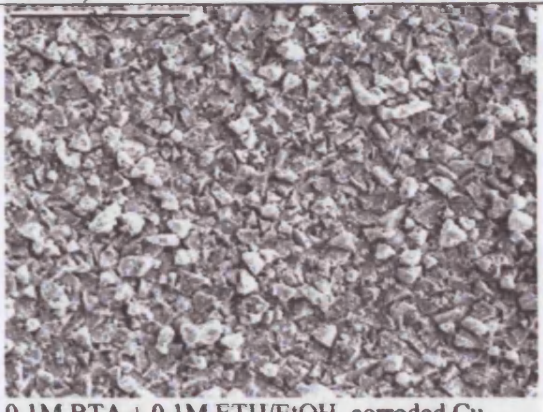
0.1M ETH/EtOH, clean Cu



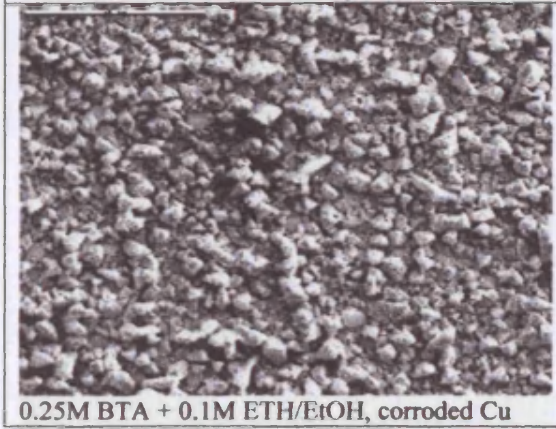
0.1M ETH/EtOH, corroded copper (etched surface)



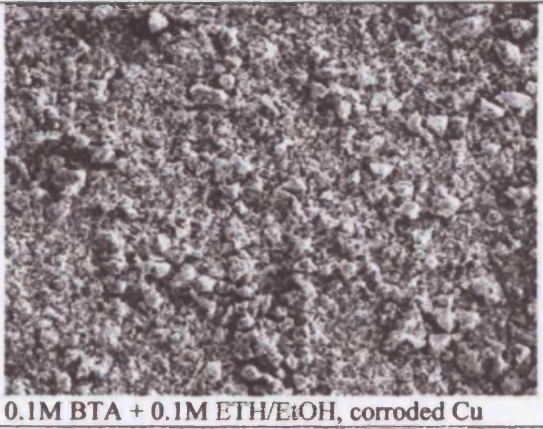
0.1M BTA + 0.1METH/EtOH, clean Cu



0.1M BTA + 0.1M ETH/EtOH, corroded Cu

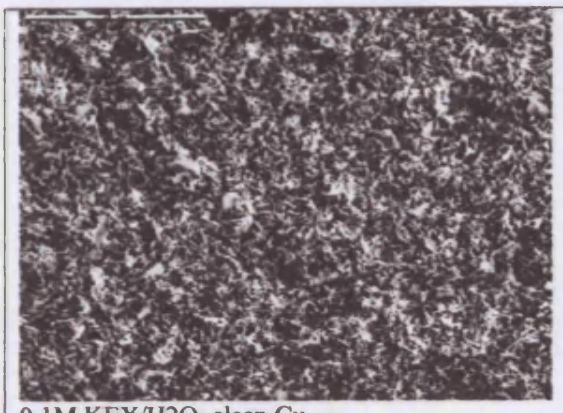


0.25M BTA + 0.1M ETH/EtOH, corroded Cu

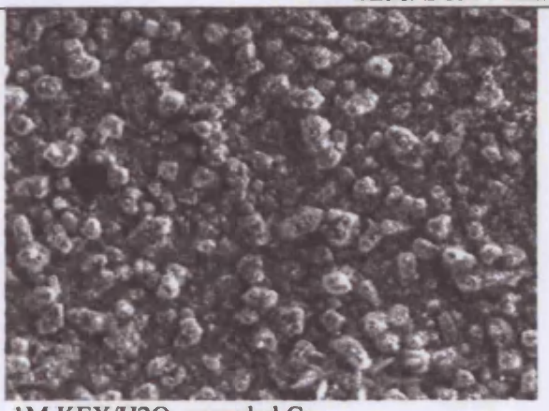


0.1M BTA + 0.1M ETH/EtOH, corroded Cu

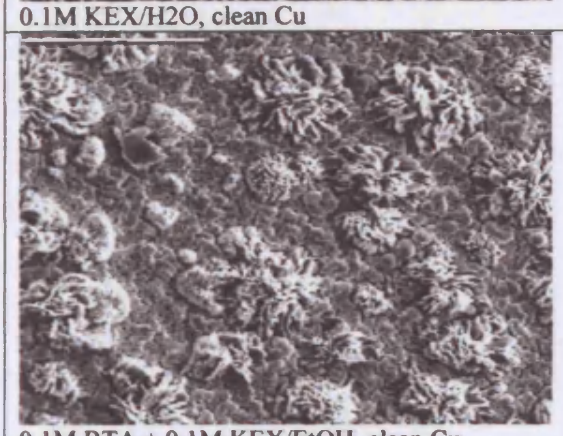
SEM: BTA + KEX



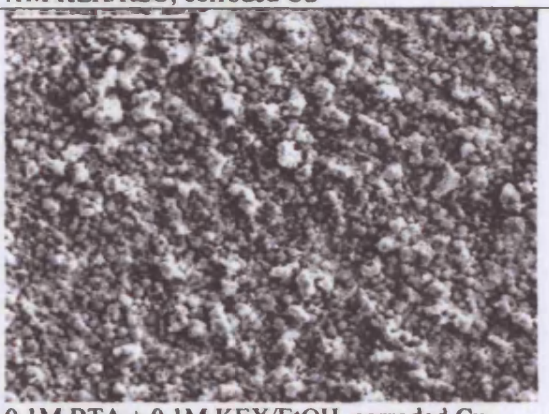
0.1M KEX/H2O, clean Cu



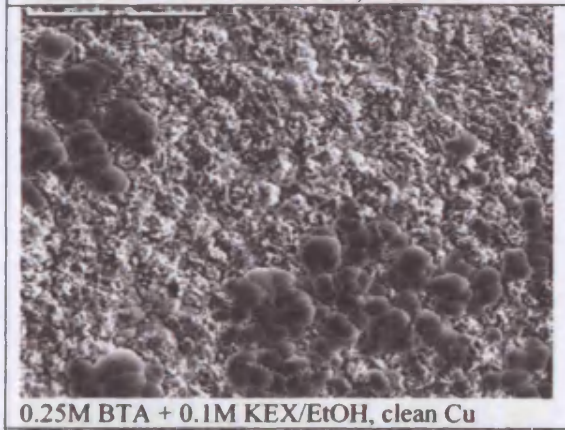
.1M KEX/H2O, corroded Cu



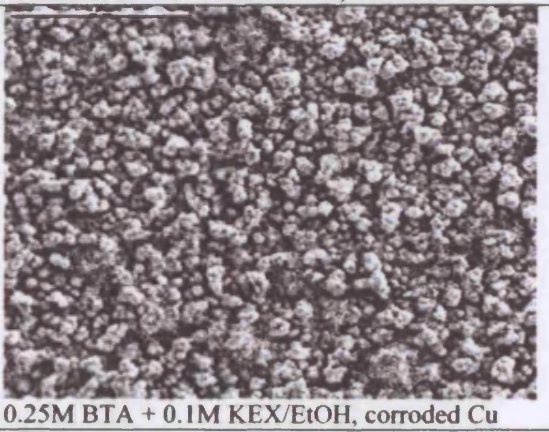
0.1M BTA + 0.1M KEX/EtOH, clean Cu



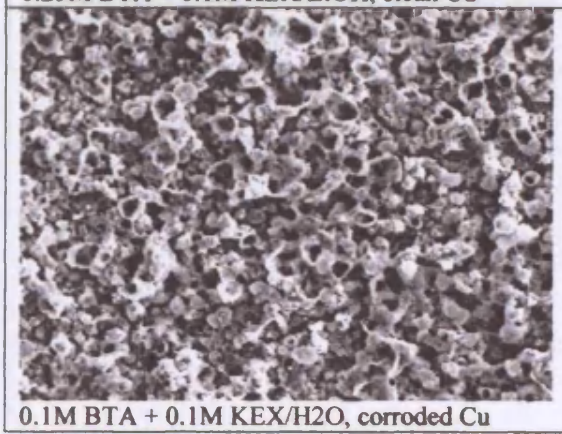
0.1M BTA + 0.1M KEX/EtOH, corroded Cu



0.25M BTA + 0.1M KEX/EtOH, clean Cu

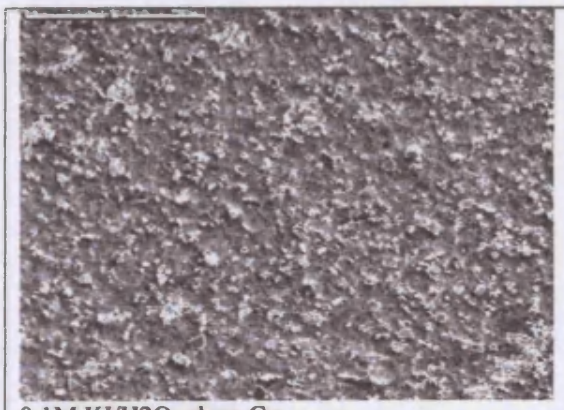


0.25M BTA + 0.1M KEX/EtOH, corroded Cu

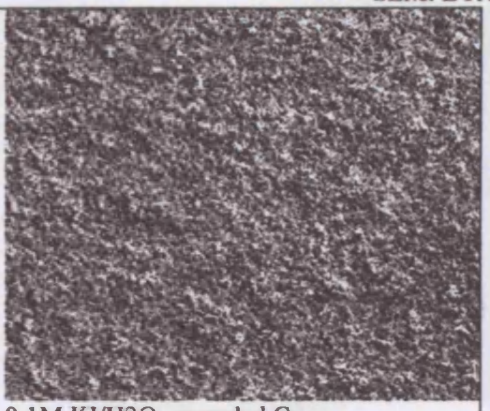


0.1M BTA + 0.1M KEX/H2O, corroded Cu

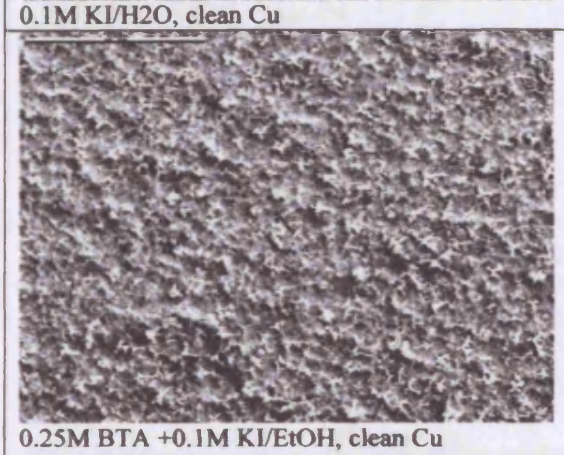
SEM: BTA + KI



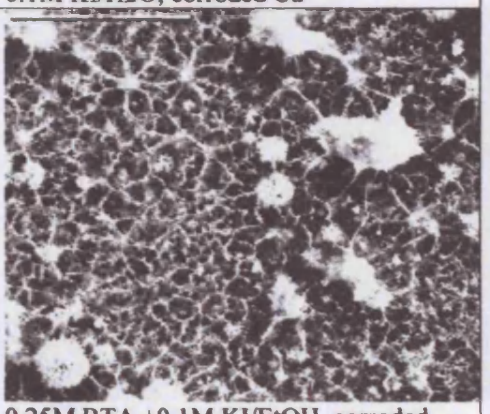
0.1M KI/H2O, clean Cu



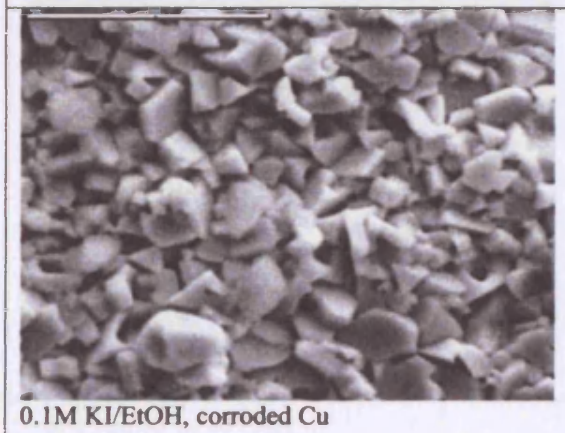
0.1M KI/H2O, corroded Cu



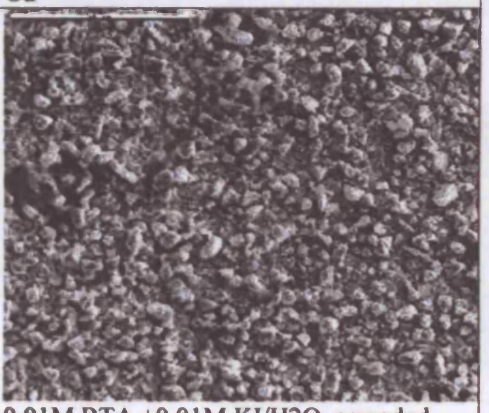
0.25M BTA +0.1M KI/EtOH, clean Cu



0.25M BTA +0.1M KI/EtOH, corroded Cu

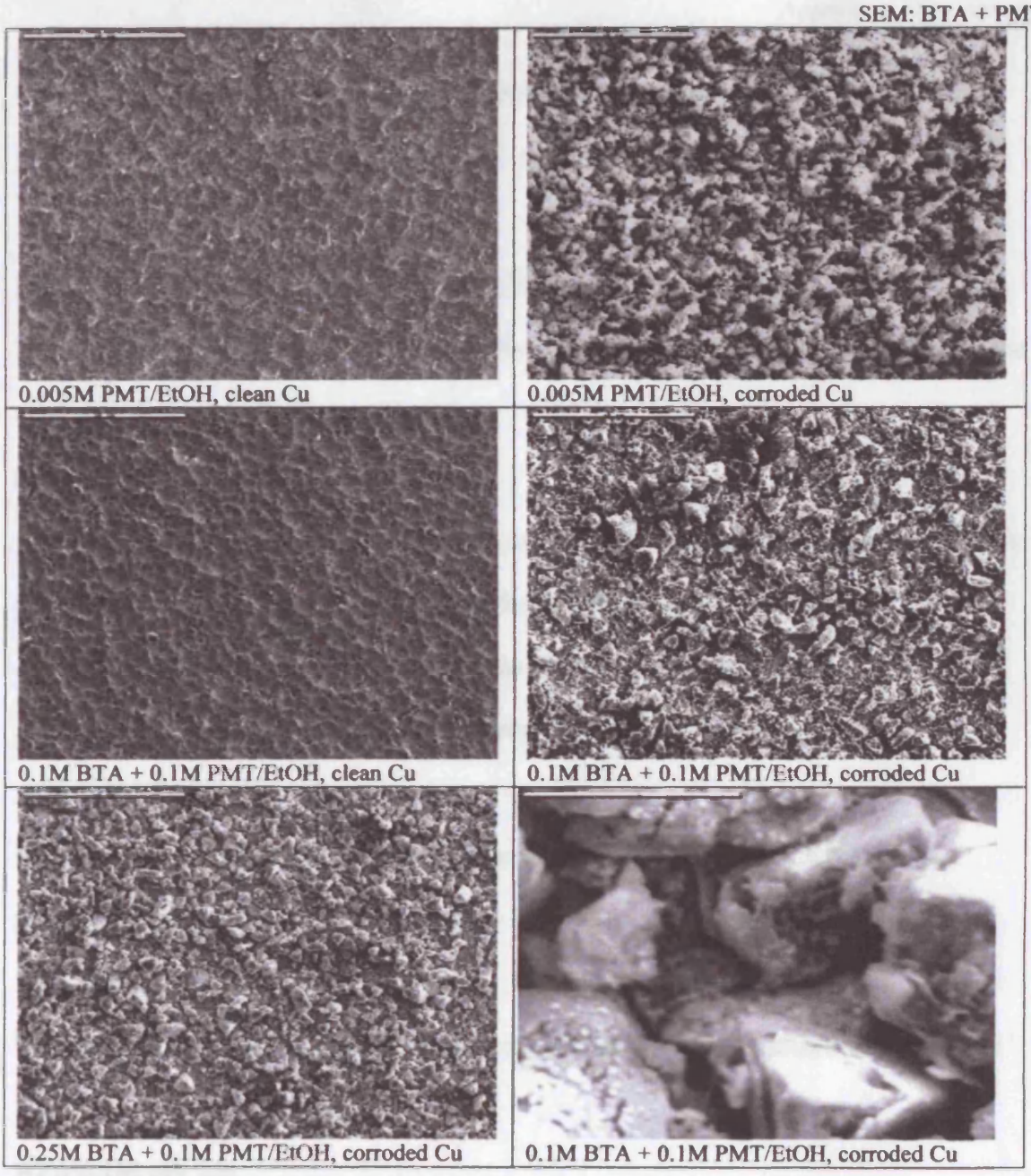


0.1M KI/EtOH, corroded Cu



0.01M BTA +0.01M KI/H2O, corroded Cu

SEM: BTA + PMT



0.005M PMT/EtOH, clean Cu

0.005M PMT/EtOH, corroded Cu

0.1M BTA + 0.1M PMT/EtOH, clean Cu

0.1M BTA + 0.1M PMT/EtOH, corroded Cu

0.25M BTA + 0.1M PMT/EtOH, corroded Cu

0.1M BTA + 0.1M PMT/EtOH, corroded Cu

Some comments on SEM-EDS linescans of BTA treatments

(see Chapter 5, section 5.6.2 and 5.6.2.1)

BTA 0.01M/H2O 1h and BTA 0.01M/EtOH

In both cases, the results showed that the nitrogen and carbon peaks overlap following the copper peak to a great extent.

BTA 0.1M/H2O 1h

As a general observation, carbon and nitrogen follow the same distribution pattern. Some small deviations found might be due to surface contamination by carbon from the atmosphere. Although, carbon and especially nitrogen follow copper, when chlorine percentages are higher, their percentages drop.

BTA 0.1M/H2O 24h

In this case, nitrogen and carbon are inversely proportional to copper, when copper percentages decreases, nitrogen and carbon increase.

BTA 0.1M-eth 1h

Interestingly, while nitrogen is inversely proportional to copper, carbon follows another pattern.

BTA 0.1M-eth 24h

Similarly, nitrogen follows copper inversely. Another interesting point is that at BTA 0.1M/H2O, 1h, the quantity of carbon and nitrogen is similar, while at longer periods of immersion and BTA in ethanol the percentages of carbon are much higher than those of nitrogen.

BTA 0.25M-eth 1h and 24 hours

The percentages of nitrogen and carbon are higher than those of copper, indicating a thicker BTA film on the surface. Nitrogen is the higher peak, inversely proportional to that of copper.

Re-used solutions of BTA

0.1M/ H2O

In all cases of coupons treated with re-used aqueous solutions of 0.1M BTA, the linescans showed that nitrogen follows inversely copper whilst carbon, although close to the nitrogen pattern, is differentiated. Generally, the linescans were found to be similar to those of coupons treated with 0.1M/ H2O for 24h by immersion.

BTA 0.1M/EtOH

The coupons treated with a solution that was re-used for another hour (Ap1-2 1h/1h) showed that carbon inversely follows copper. Nitrogen presents a similar picture to carbon with some variations.

In case of copper treated by 24-hour immersion with solution that had been re-used for a another 24 hour the linescan showed that carbon and nitrogen were at higher percentages than copper. Nitrogen is inversely proportional to copper. Carbon follows nitrogen but to a lesser extent.

BTA solutions of 0.25M/EtOH

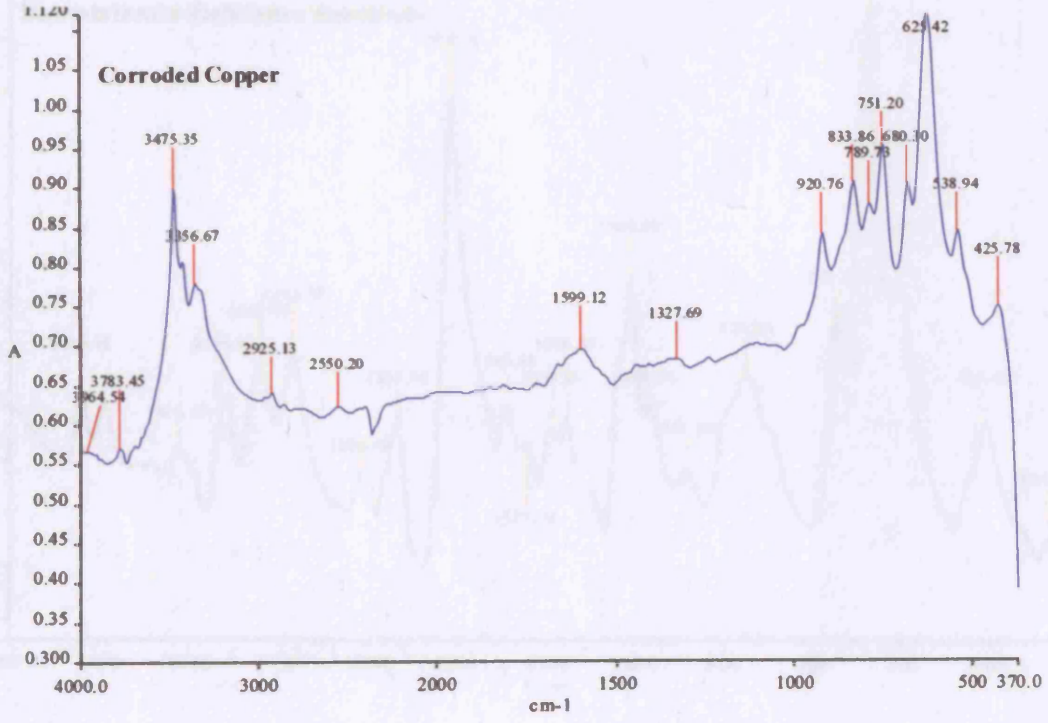
When copper treated for an hour with solution that was re-used for another hour the results showed that carbon inversely follows copper. Nitrogen also follows copper but to a lesser extent. The percentages of carbon, nitrogen and copper were similar.

In case of treatment of copper by 24-hour immersion in a solution that had been used for a further 24 hours, the coupons presented different phases on the surface. On top of the

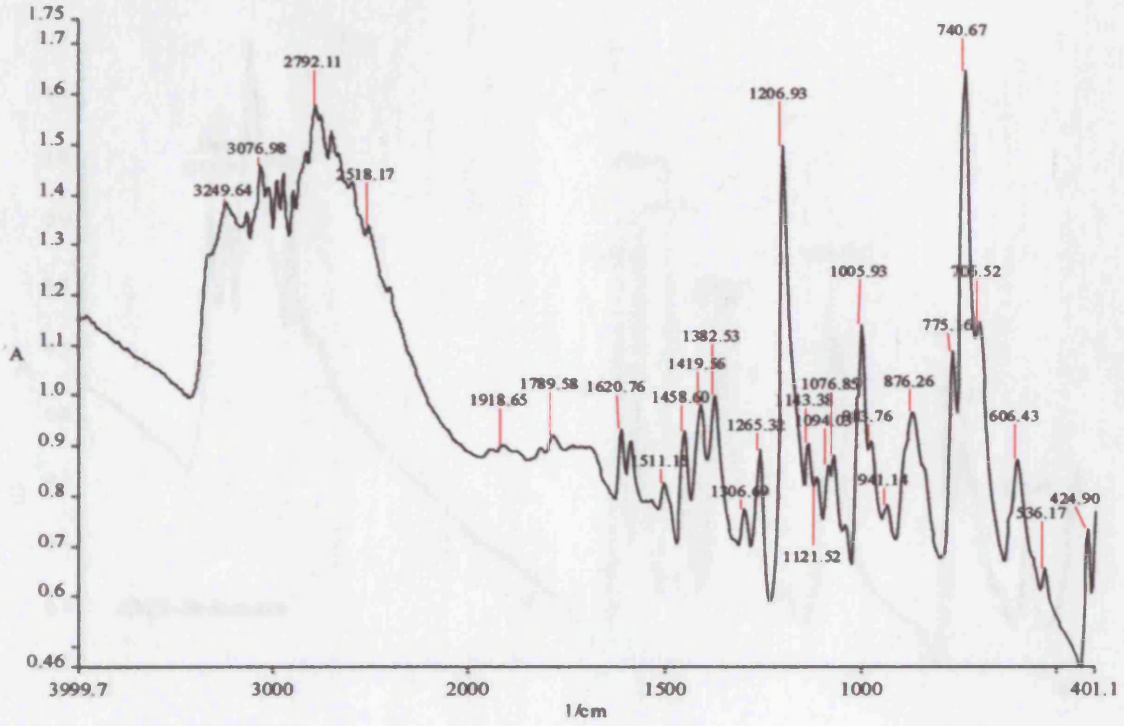
surface a darker precipitant was found on some areas. The linescans were carried out on both areas. The results were similar for the darker and light parts. Carbon followed inversely copper. Nitrogen also followed inversely copper but to a lesser extent.

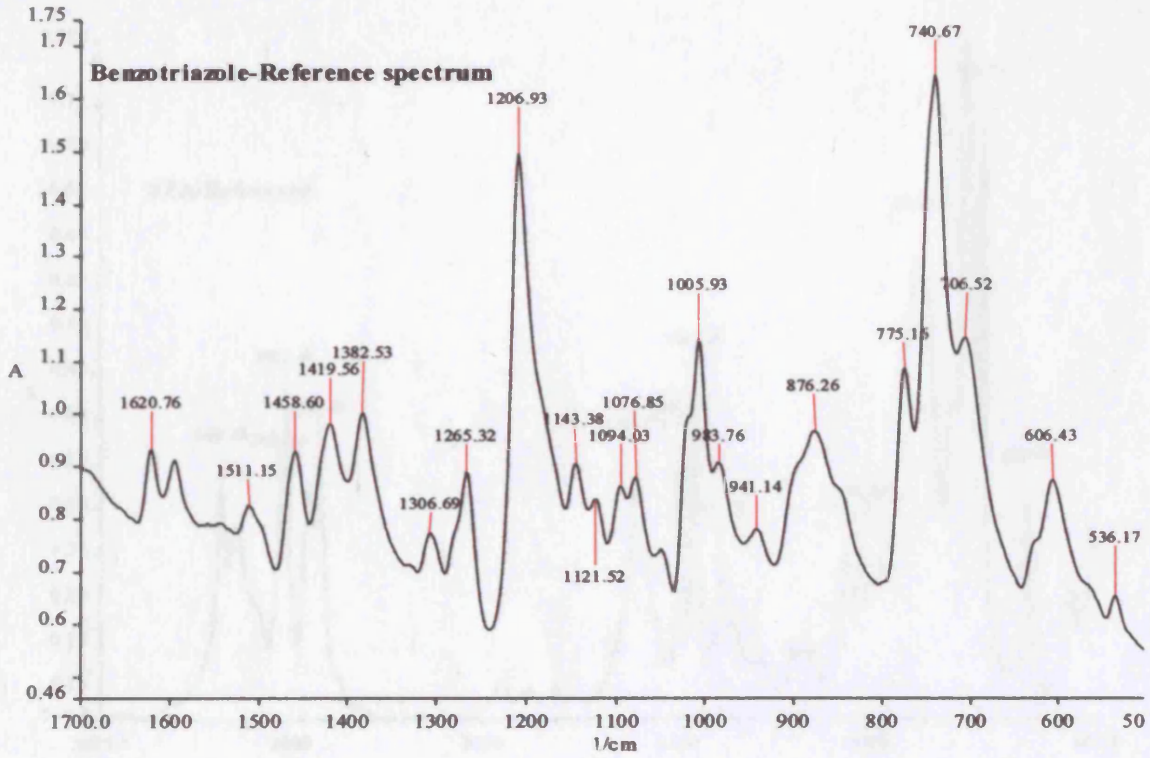
Appendix 5

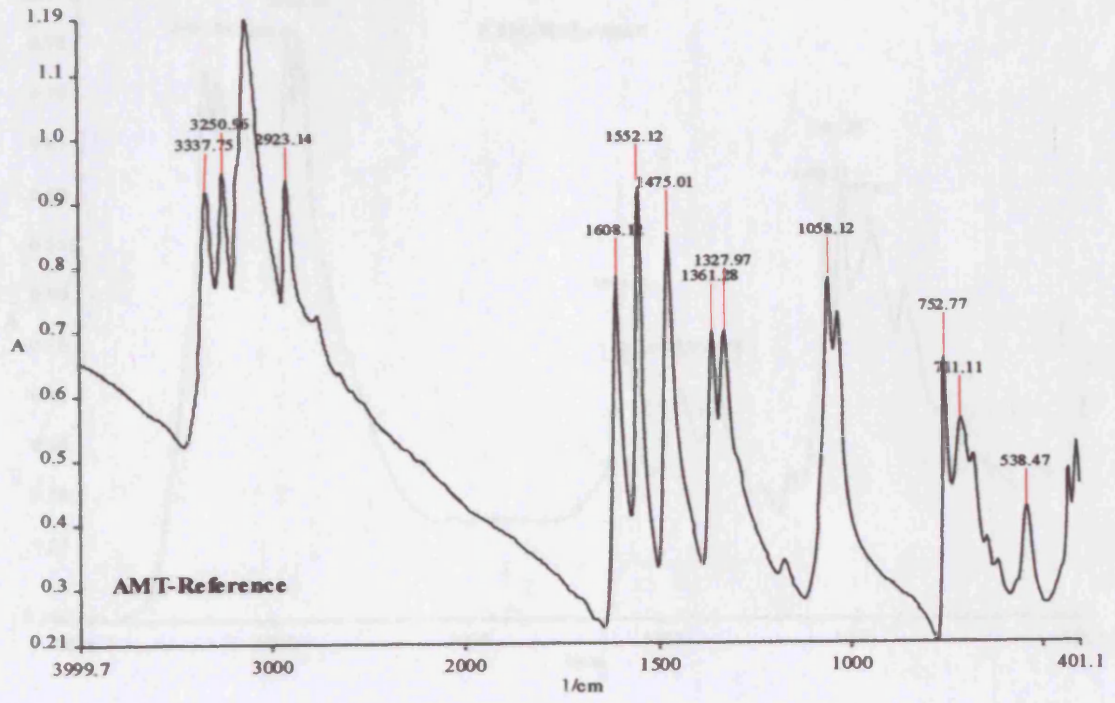
FTIR: Reference Spectra

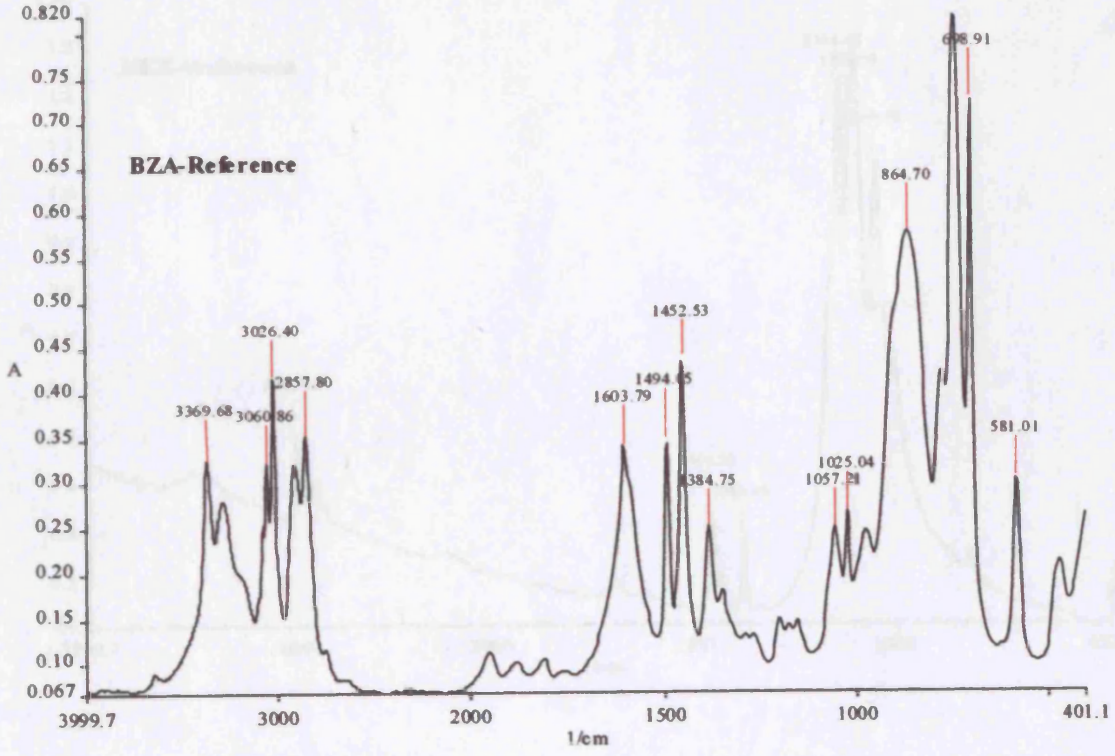


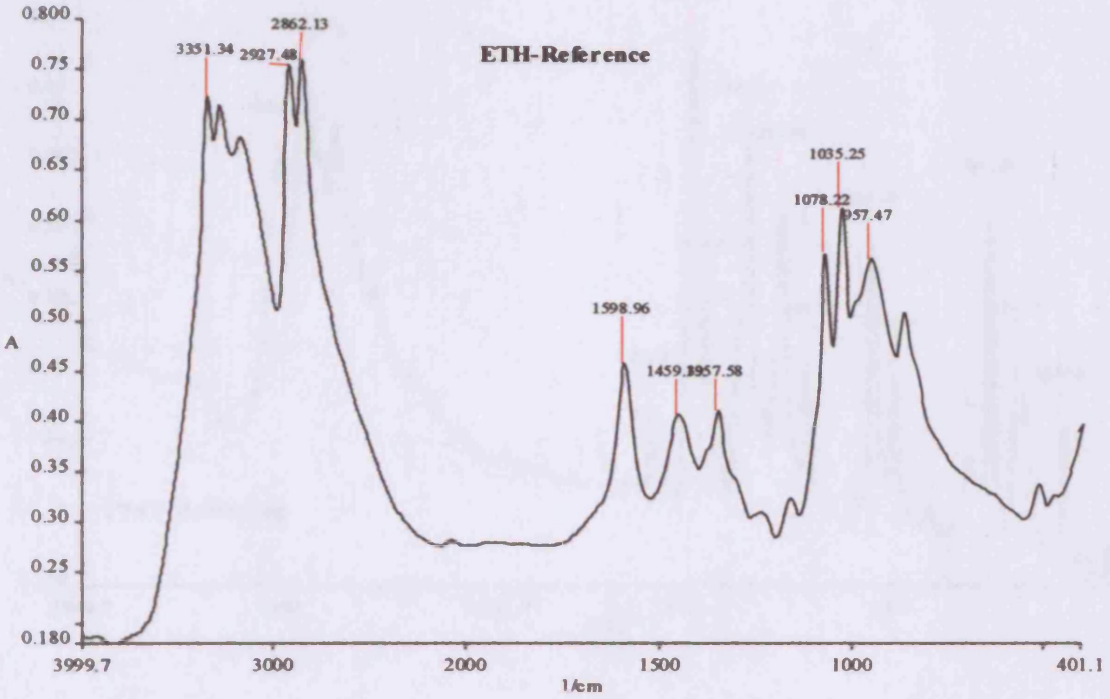
BTA-Reference

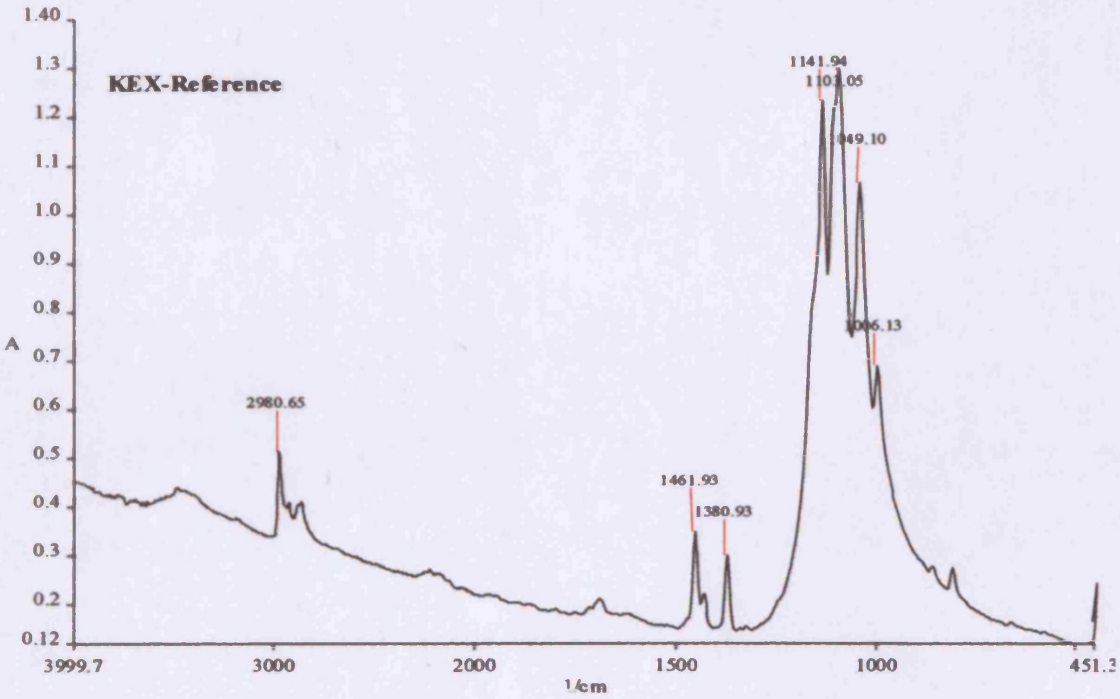


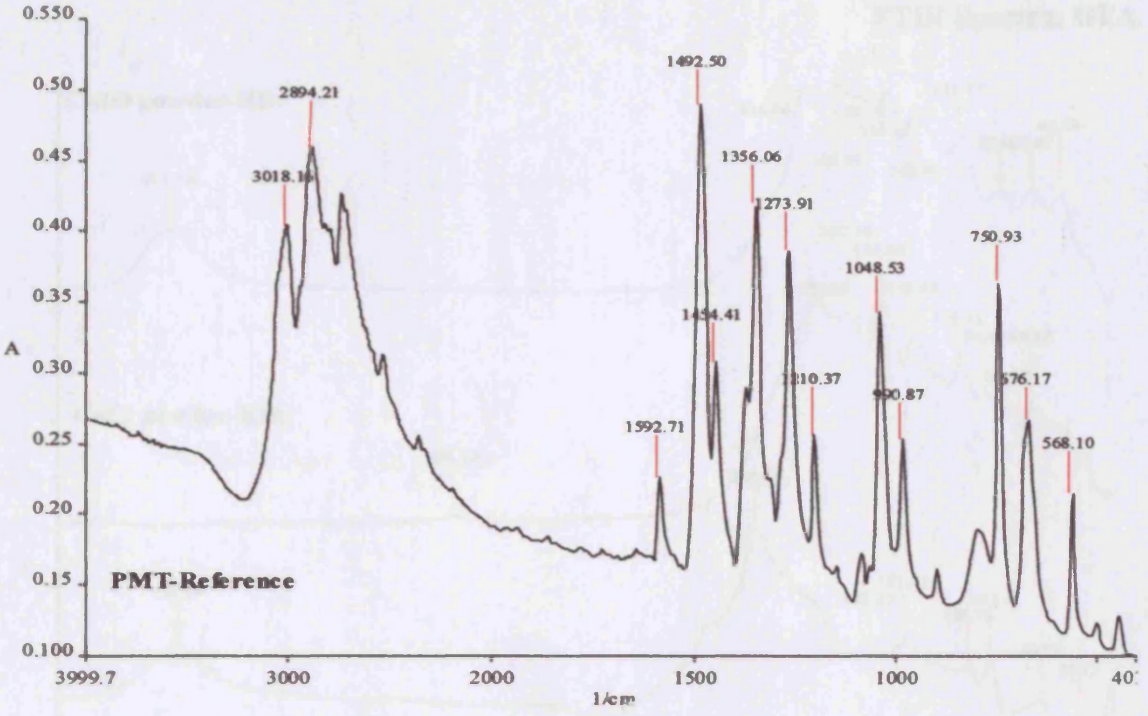



AMT-Reference
A
1/cm
3337.75
3250.95
2923.14
1552.12
1475.01
1608.12
1327.97
1361.28
1058.12
752.77
731.11
538.47

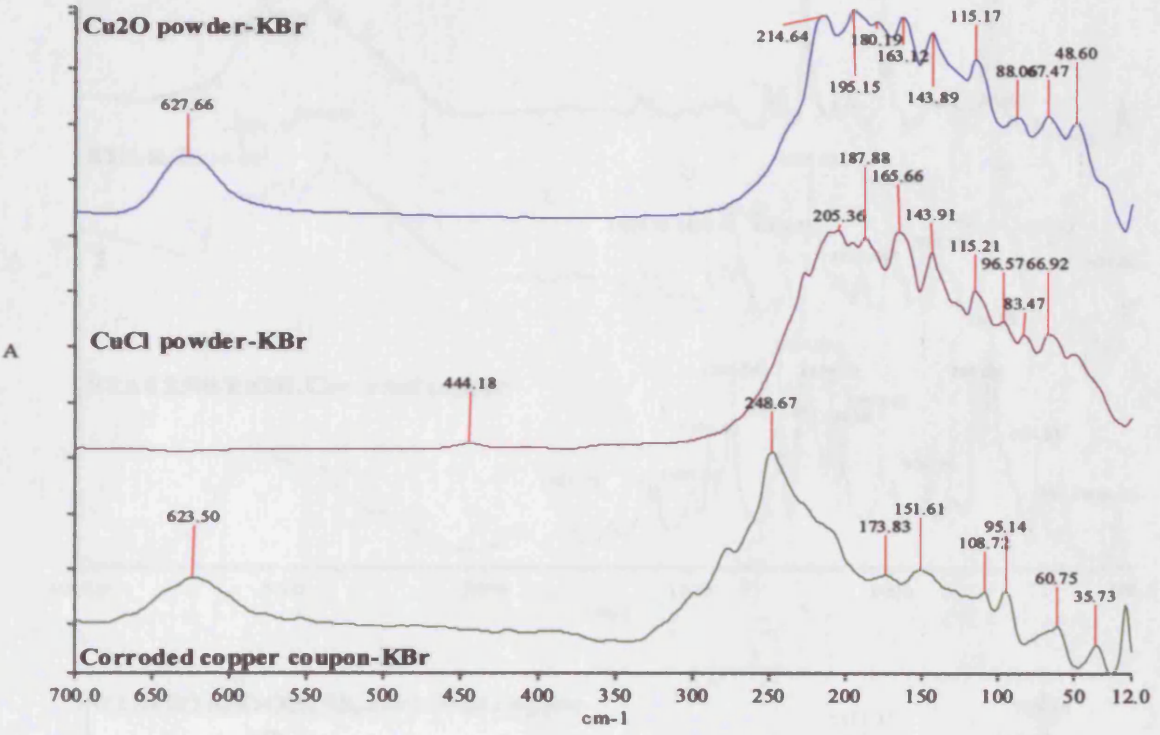

BZA-Reference
A
1/cm
3369.68
3060.86
3026.40
2857.80
1603.79
1494.65
1452.53
1384.75
1057.21
1025.04
864.70
698.91
581.01

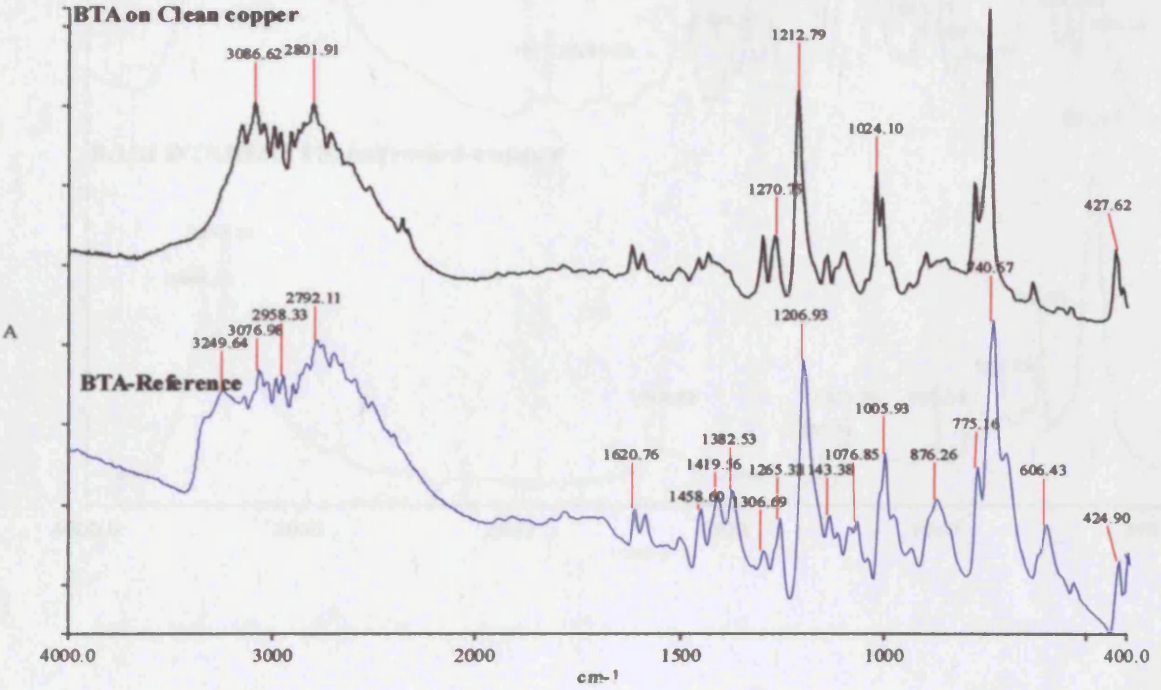

ETH-Reference
3351.34
2927.48
2862.13
1598.96
1459.39
1457.58
1078.22
1035.25
957.47
A
1/cm

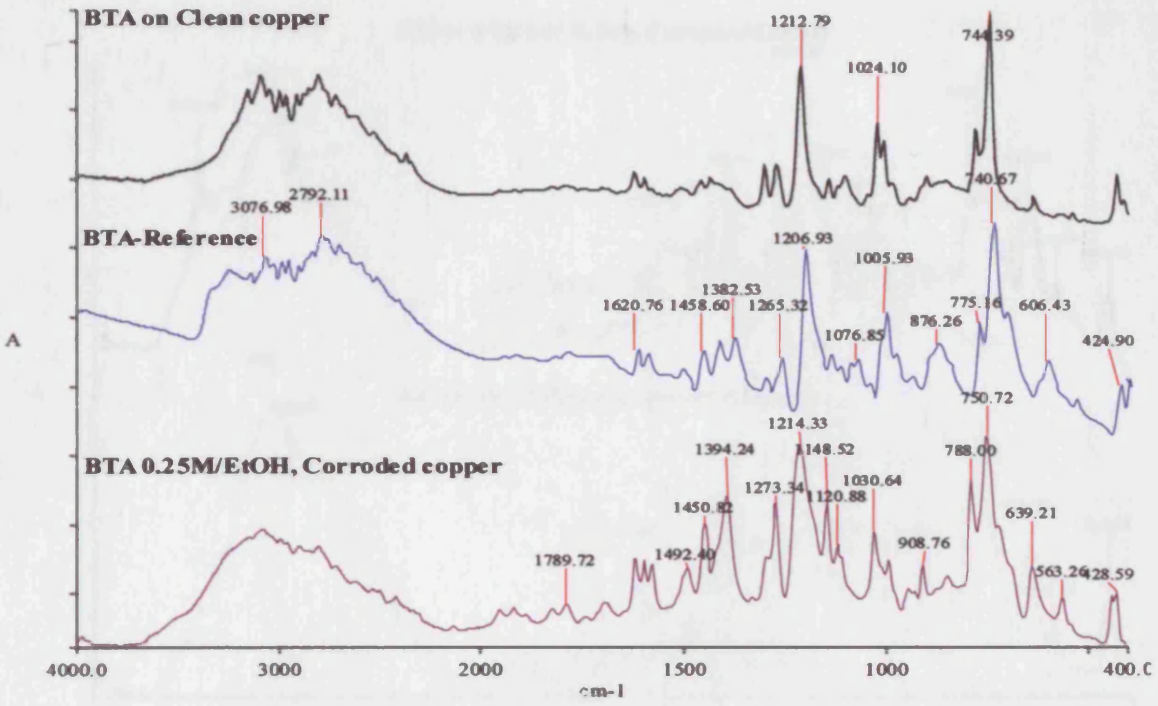

KEX-Reference
2980.65
1461.93
1380.93
1141.94
1103.05
1049.10
1006.13
A
1/cm

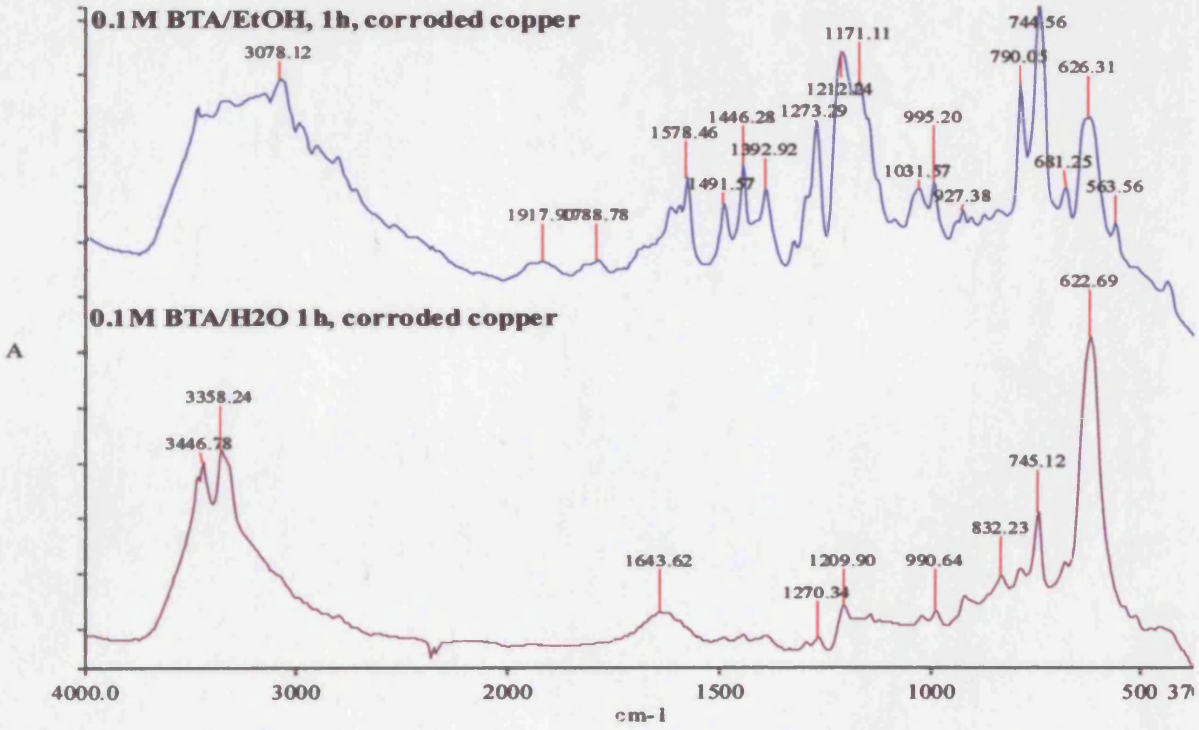

0.550
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.100
A
2894.21
3018.16
1492.50
1356.06
1273.91
1048.53
750.93
1454.41
1592.71
1310.37
950.87
576.17
568.10
PMT-Reference
3999.7
3000
2000
1500
1000
1/cm

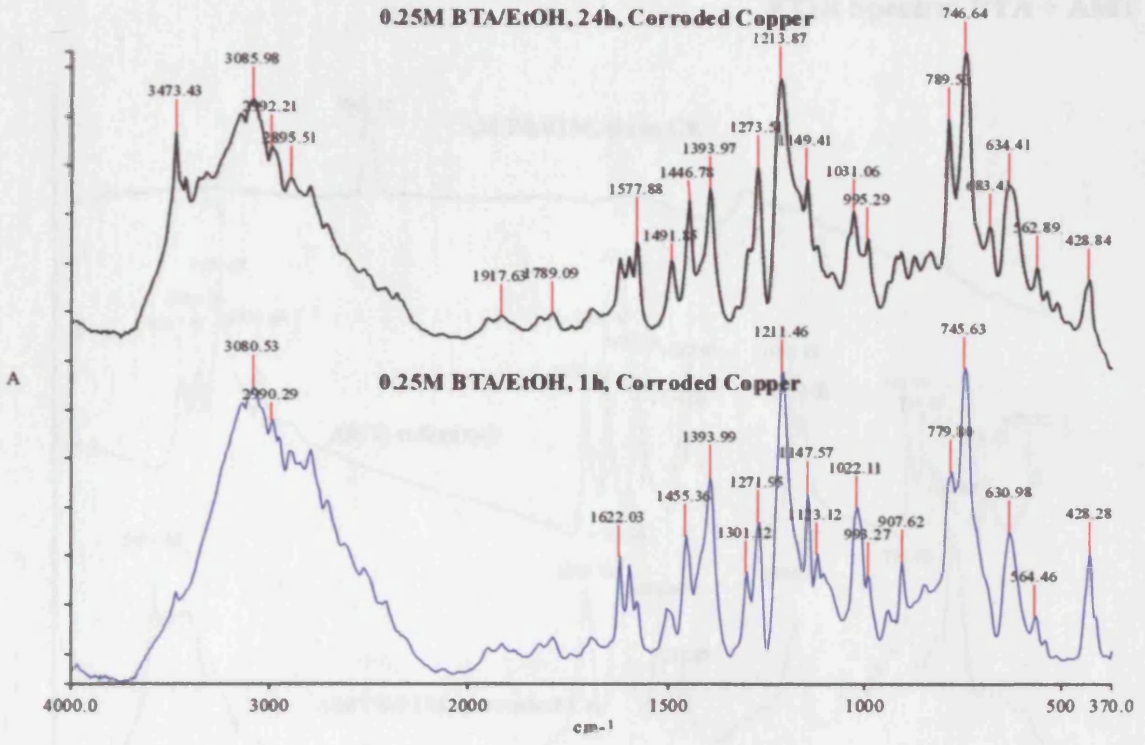
FTIR Spectra: BTA



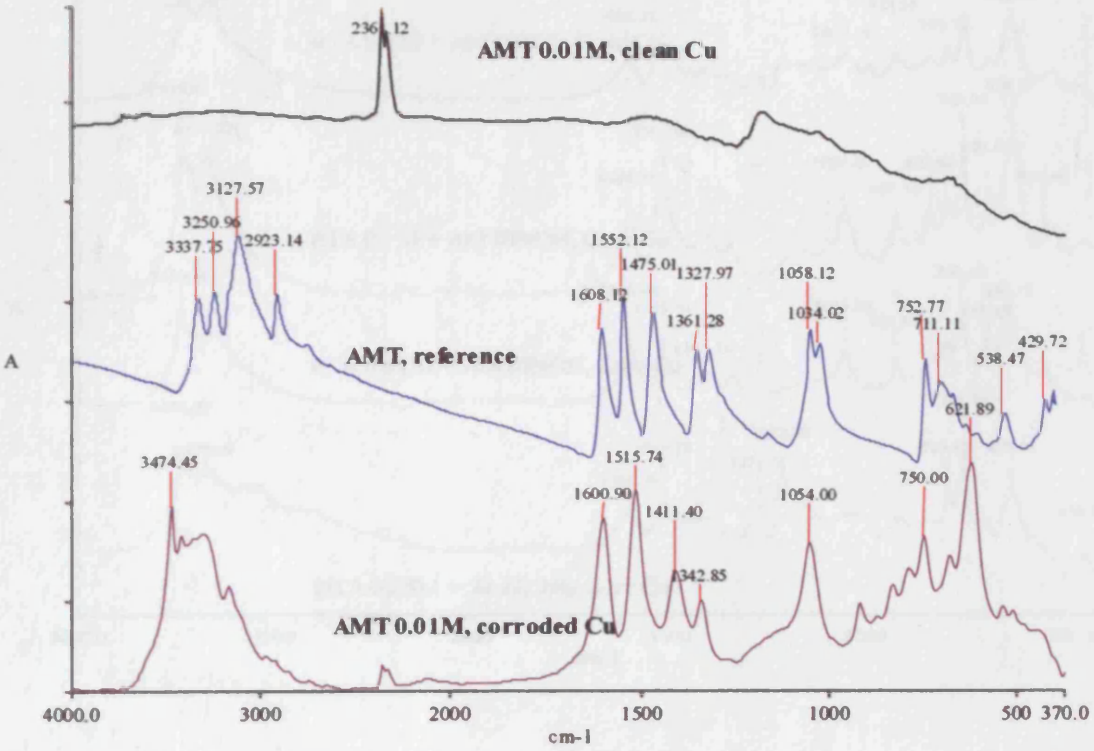


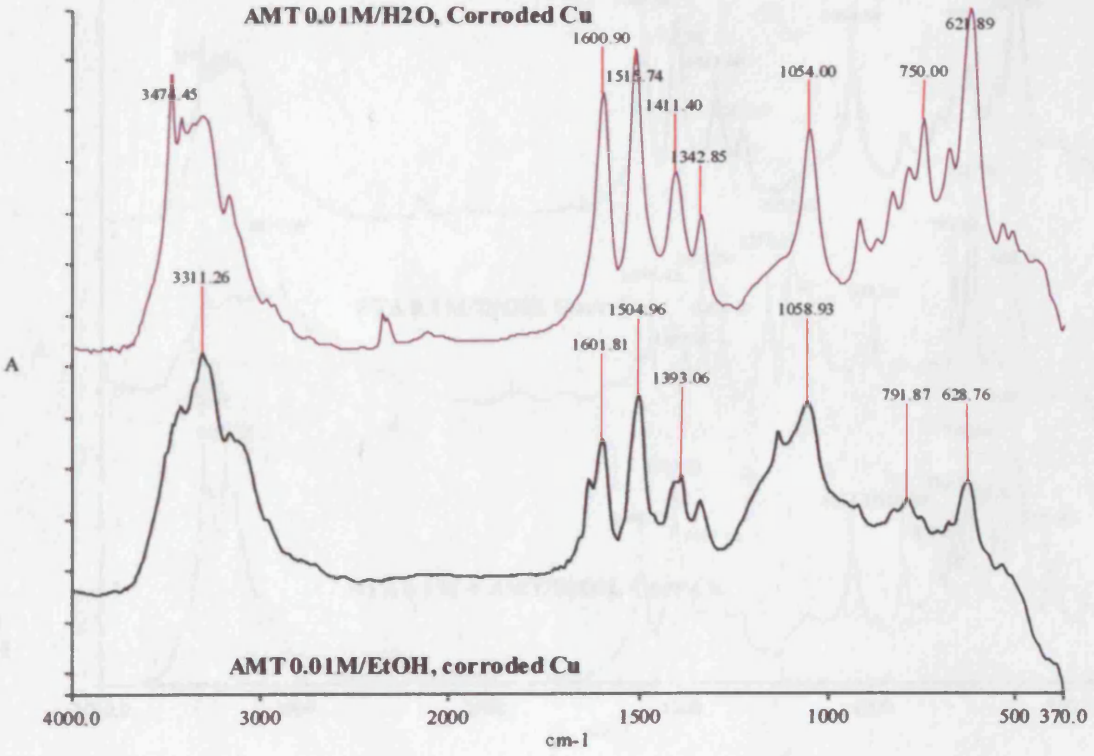

BTA on Clean copper
1212.79
1024.10
744.39
740.67
BTA-Reference
3076.98
2792.11
1206.93
1005.93
1620.76
1458.60
1382.53
1265.32
1076.85
876.26
775.16
606.43
424.90
750.72
BTA 0.25M/EtOH, Corroded copper
1214.33
1394.24
1148.52
788.00
1273.34
1030.64
1120.88
1450.82
639.21
908.76
1789.72
1492.40
563.26
428.59
A
4000.0
3000
2000
1500
1000
400.0
cm-1

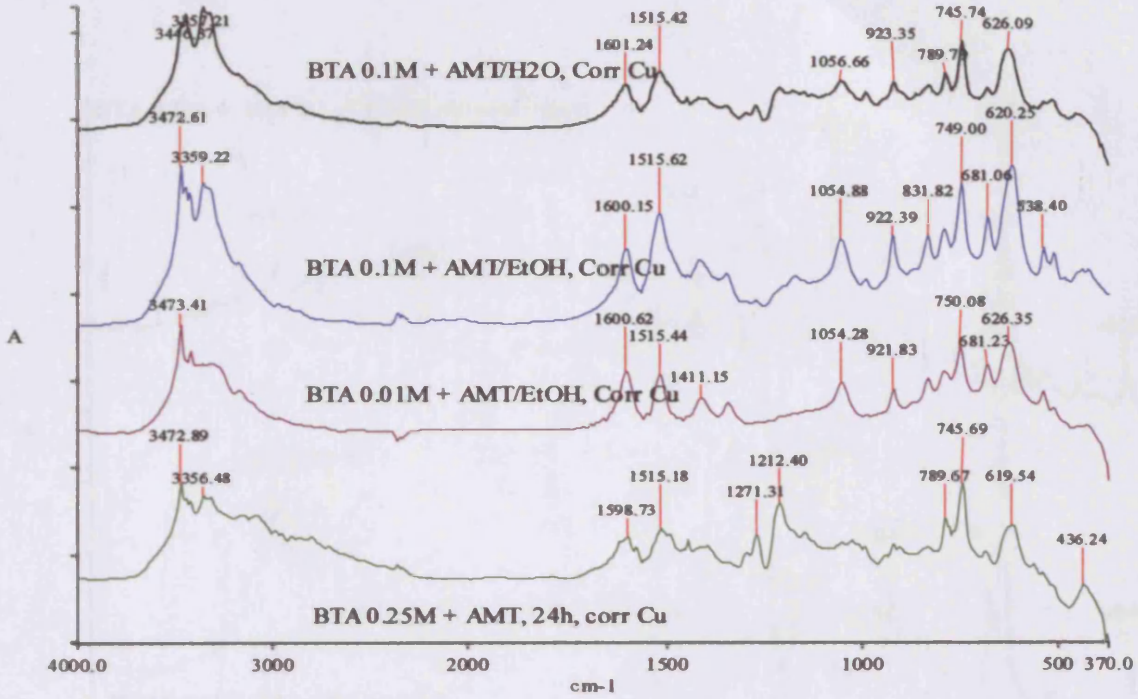

0.1 M BTA/EtOH, 1h, corroded copper
3078.12
1171.11
744.56
790.05
626.31
1212.24
1273.29
1446.28
995.20
1578.46
1392.92
1031.57
681.25
1491.57
927.38
563.56
1917.90
788.78
0.1 M BTA/H2O 1 h, corroded copper
622.69
A
3358.24
3446.78
745.12
832.23
1643.62
1209.90
990.64
1270.34
4000.0
3000
2000
1500
1000
500
cm-1

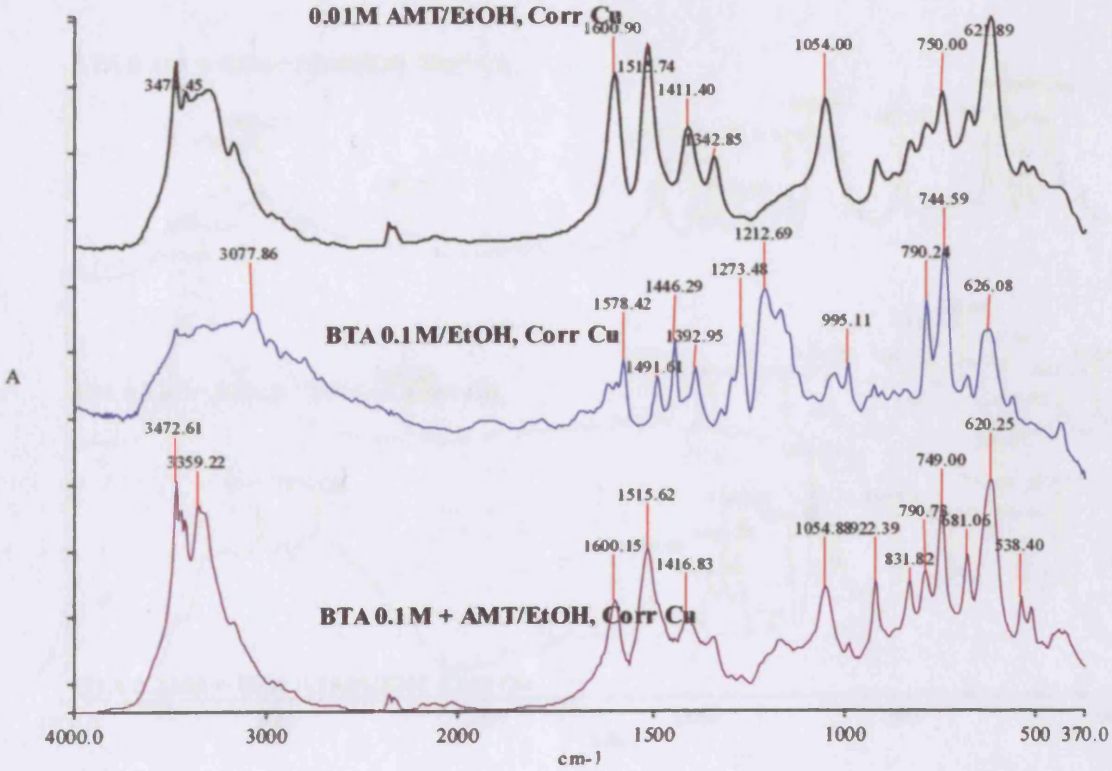

0.25M BTA/EtOH, 24h, Corroded Copper
3473.43
3085.98
2892.21
2895.51
1917.63
1789.09
1577.88
1491.85
1446.78
1393.97
1273.58
1213.87
1149.41
1031.06
995.29
746.64
789.55
634.41
583.41
562.89
428.84
0.25M BTA/EtOH, 1h, Corroded Copper
3080.53
2990.29
1622.03
1455.36
1393.99
1301.12
1271.95
1211.46
1147.57
1123.12
1022.11
998.27
907.62
745.63
779.80
630.98
564.46
428.28
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

FTIR Spectra: BTA + AMT

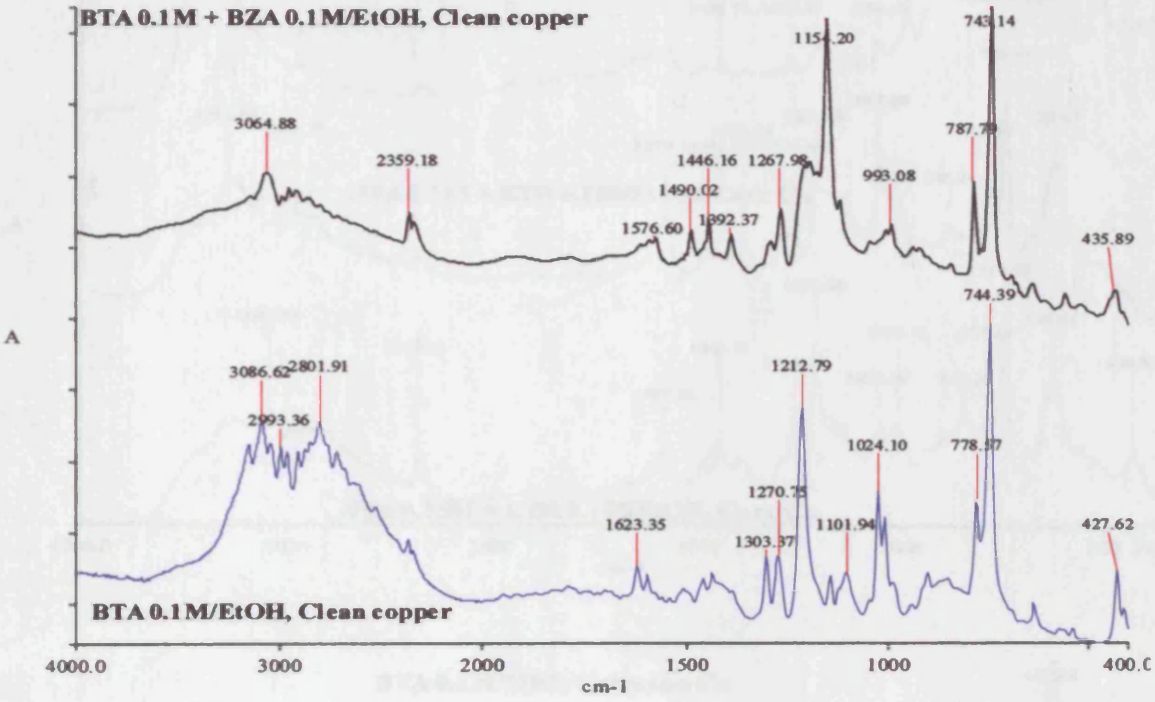


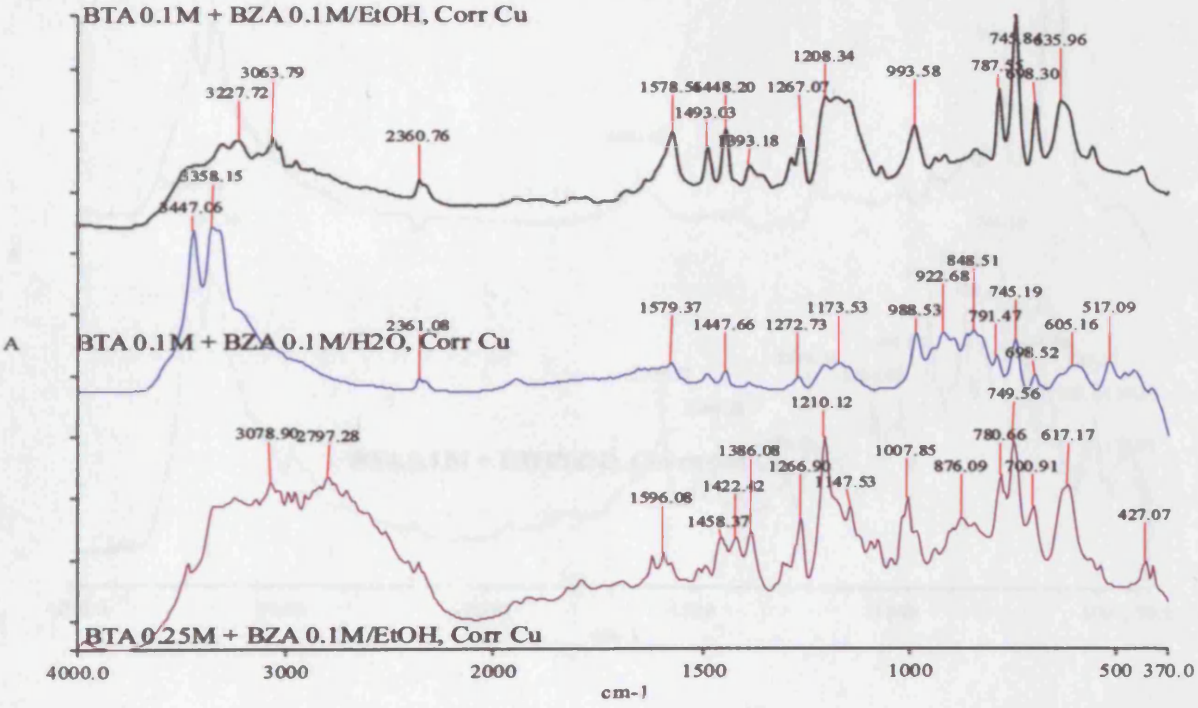



BTA 0.1M + AMT/H2O, Corr Cu
BTA 0.1M + AMT/EtOH, Corr Cu
BTA 0.01M + AMT/EtOH, Corr Cu
BTA 0.25M + AMT, 24h, corr Cu
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

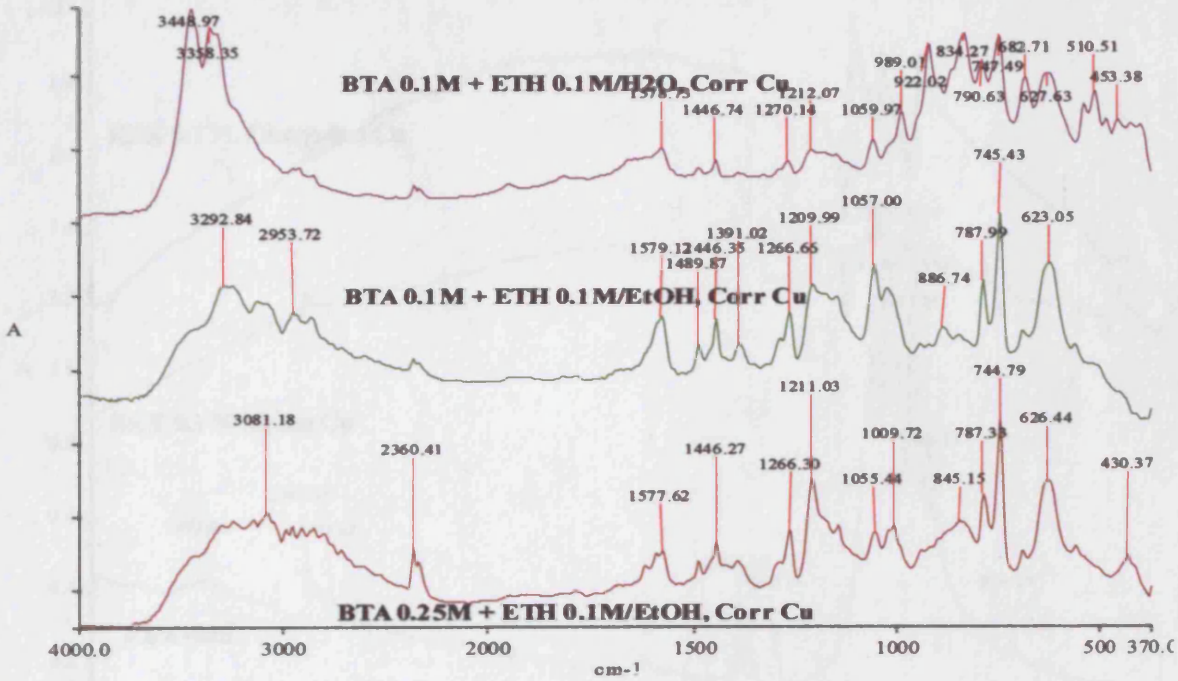

0.01M AMT/EtOH, Corr Cu
BTA 0.1M/EtOH, Corr Cu
BTA 0.1M + AMT/EtOH, Corr Cu
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

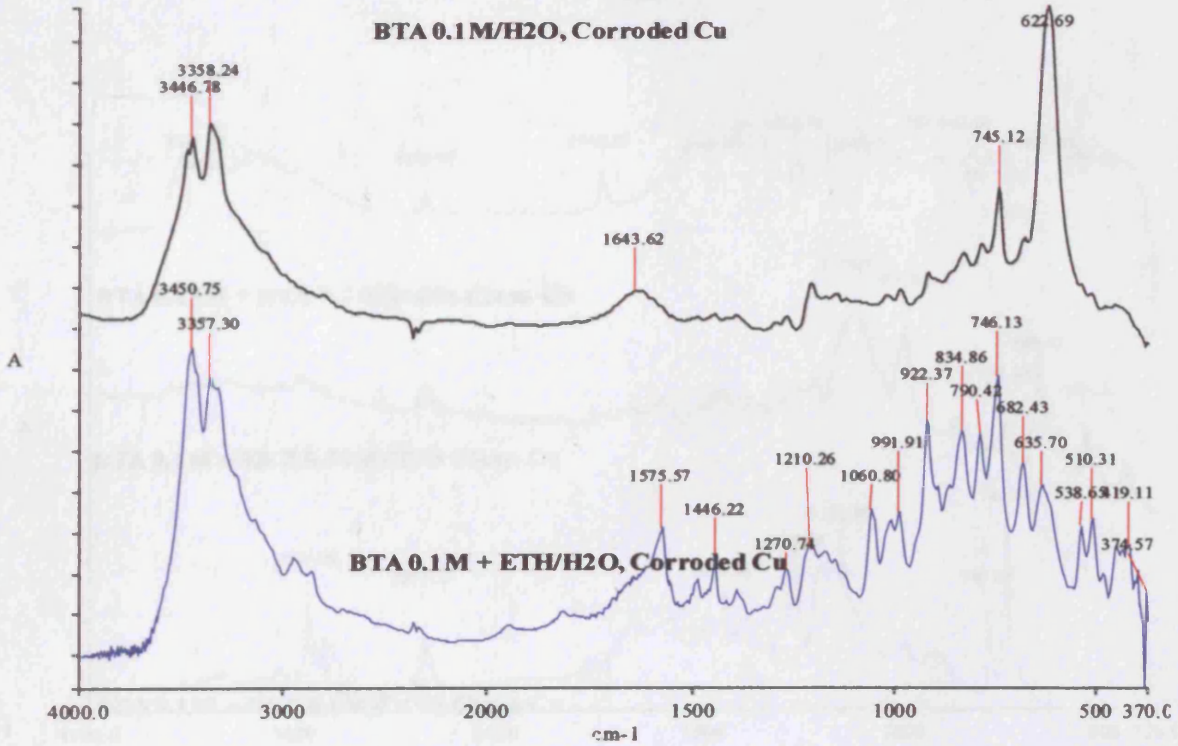
FTIR Spectra: BTA + BZA

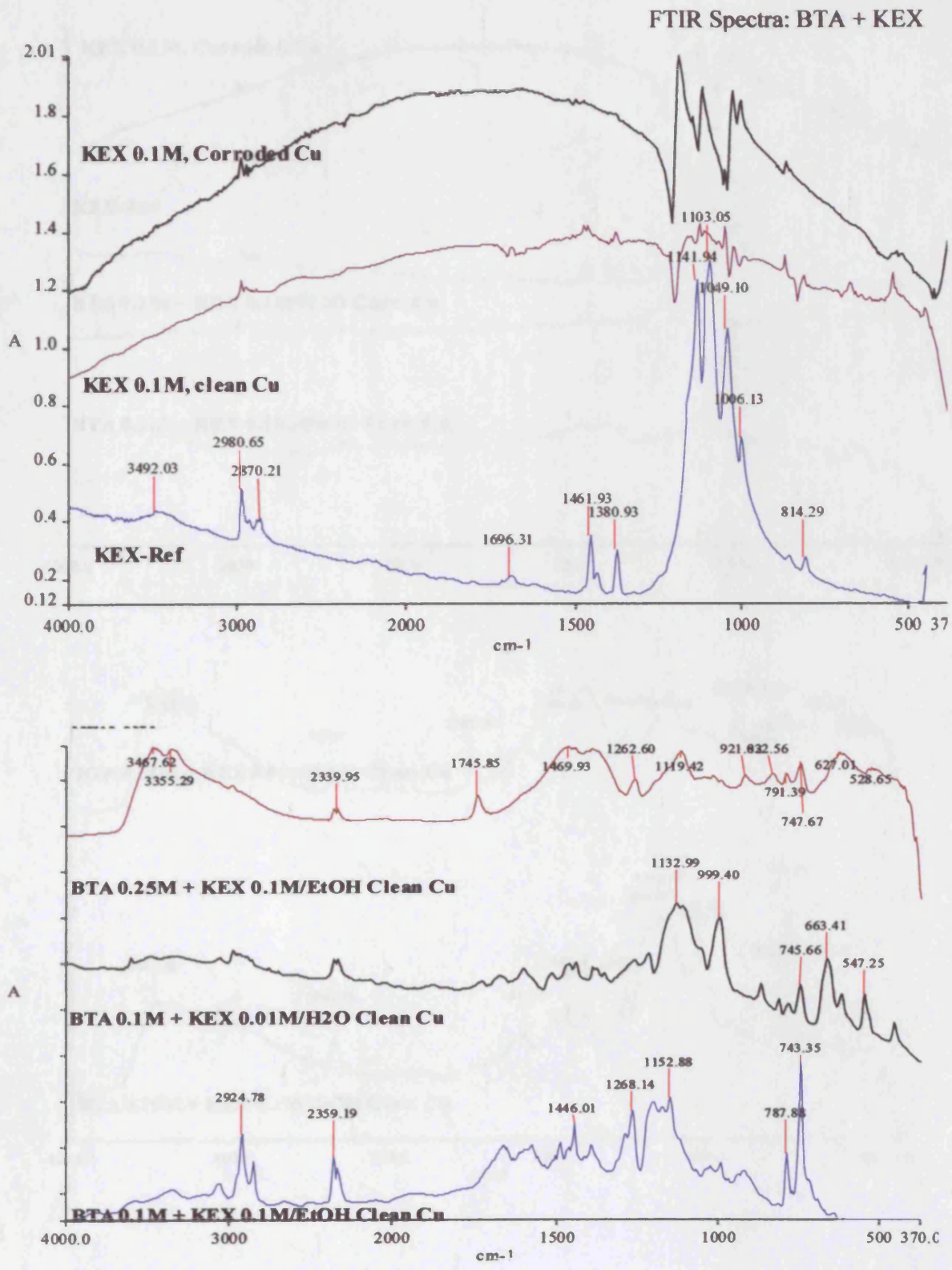


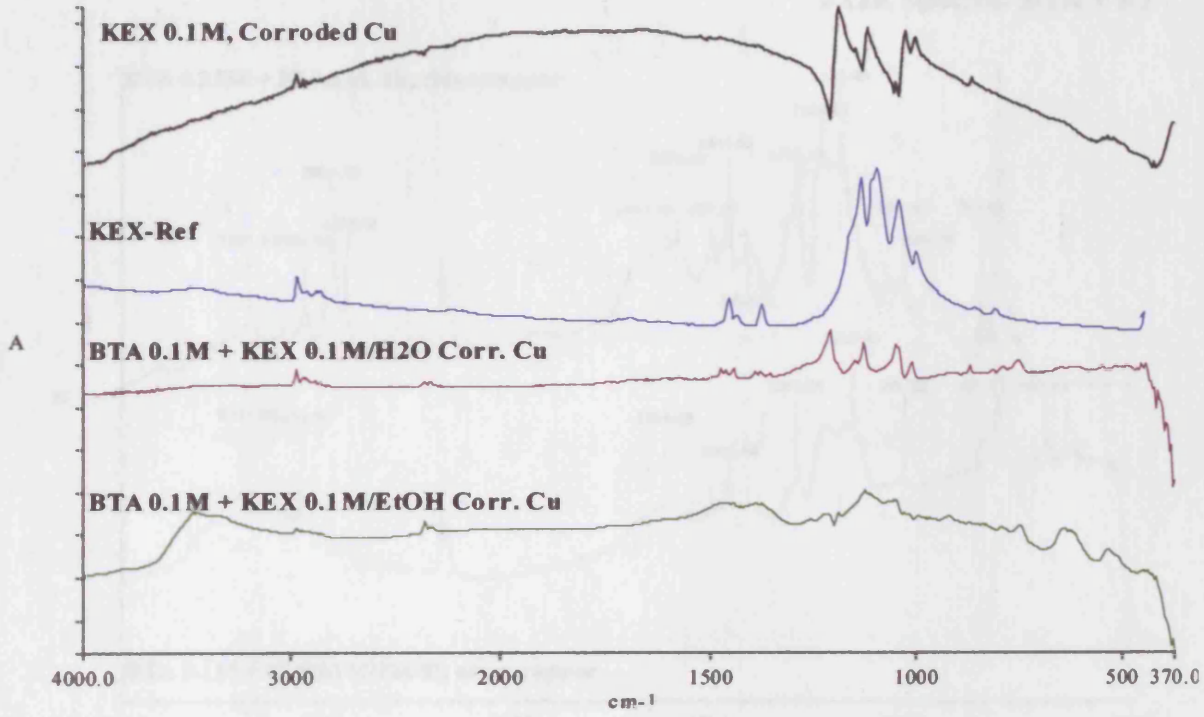


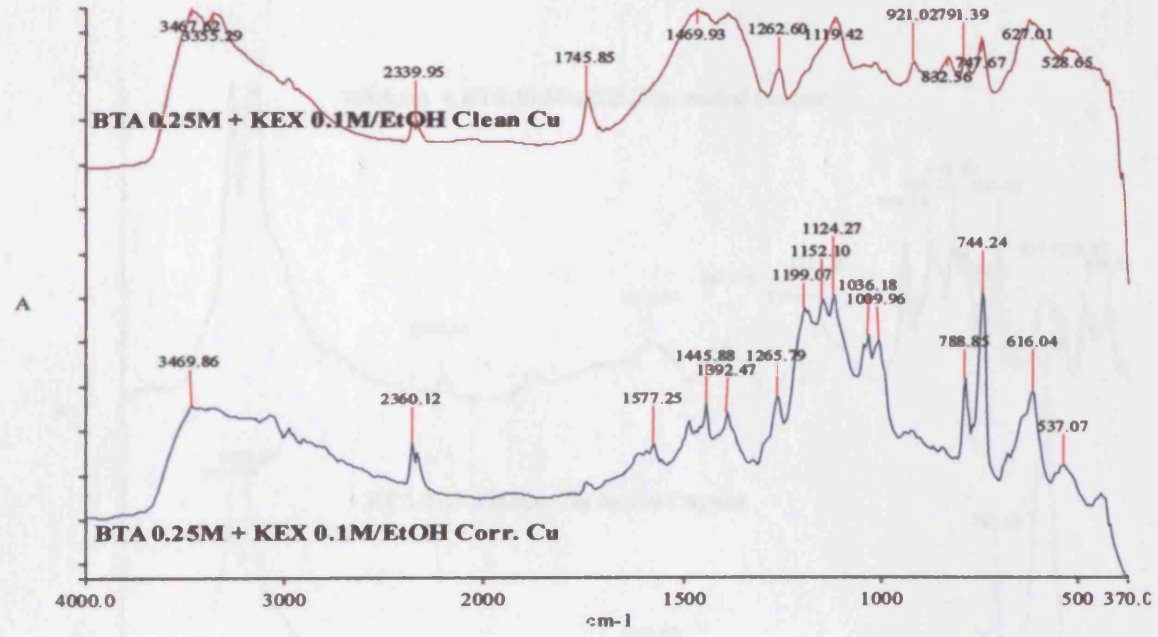
FTIR Spectra: BTA + ETH



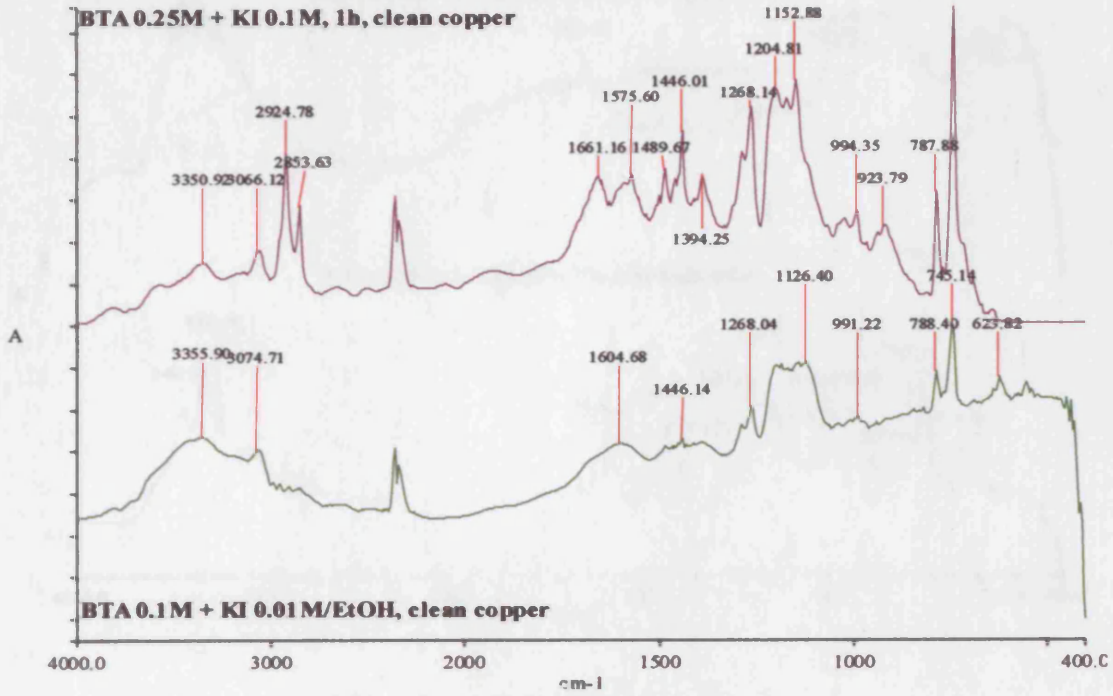


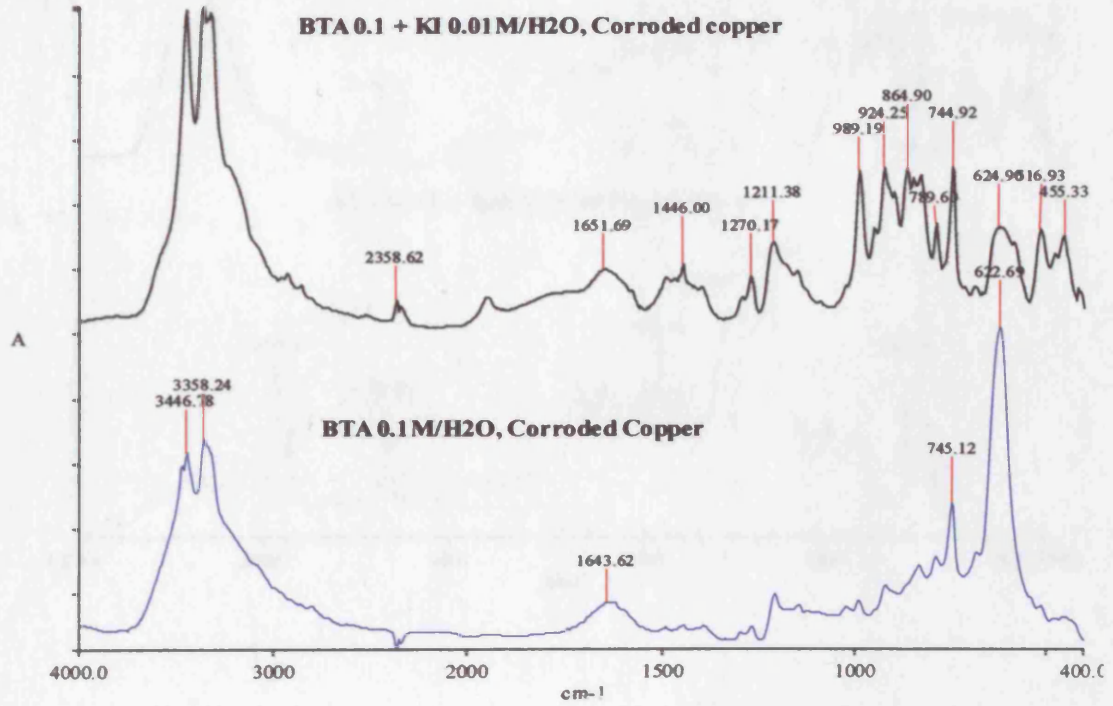

FTIR Spectra: BTA + KEX
KEX 0.1M, Corroded Cu
KEX 0.1M, clean Cu
KEX-Ref
BTA 0.25M + KEX 0.1M/EtOH Clean Cu
BTA 0.1M + KEX 0.01M/H2O Clean Cu
BTA 0.1M + KEX 0.1M/EtOH Clean Cu
A
cm-1
4000.0
3000
2000
1500
1000
500
2.01
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.12
3492.03
2980.65
2870.21
1696.31
1461.93
1380.93
1103.05
1141.94
1049.10
1006.13
814.29
3467.62
3355.29
2339.95
1745.85
1469.93
1262.60
1119.42
791.39
747.67
627.01
528.65
1132.99
999.40
745.66
663.41
547.25
2924.78
2359.19
1446.01
1268.14
1152.88
787.88
743.35

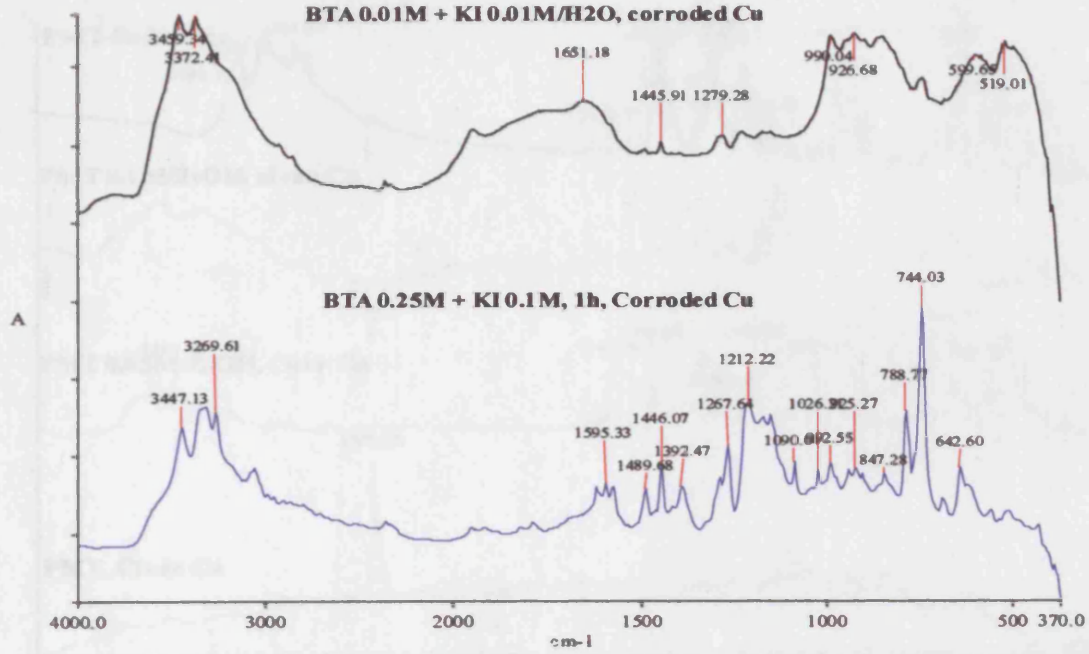

KEX 0.1M, Corroded Cu
KEX-Ref
BTA 0.1M + KEX 0.1M/H2O Corr. Cu
BTA 0.1M + KEX 0.1M/EtOH Corr. Cu
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

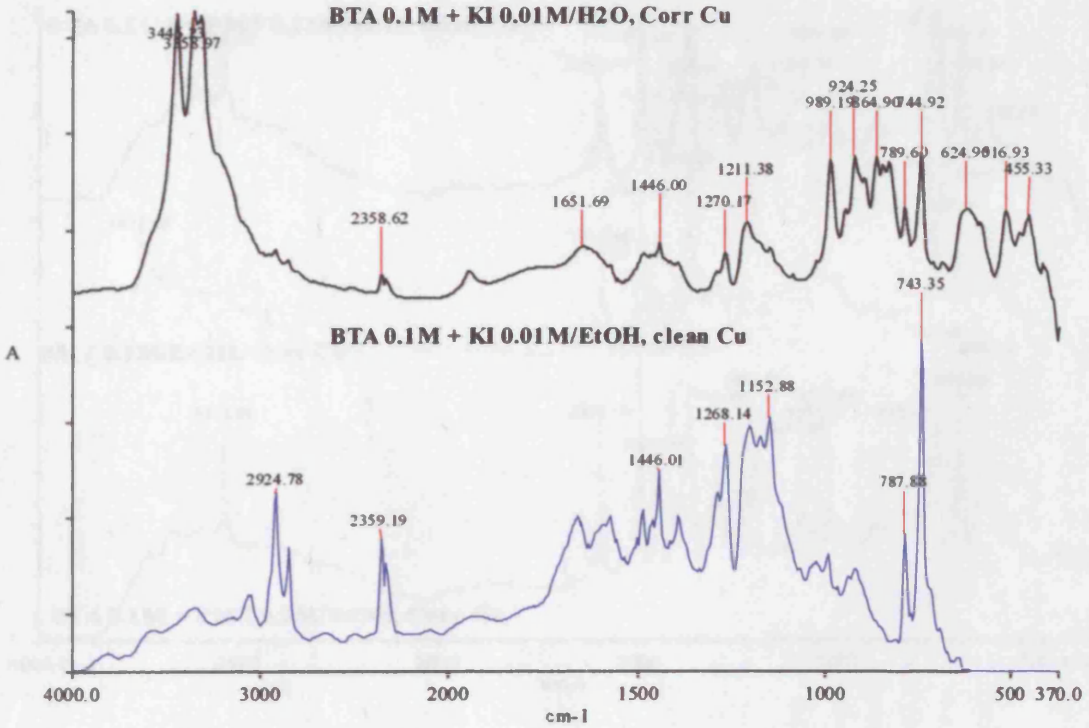

3467.82
3353.29
2339.95
1745.85
1469.93
1262.60
1119.42
921.02
791.39
627.01
832.56
787.67
528.65
BTA 0.25M + KEX 0.1M/EtOH Clean Cu
1124.27
1152.10
1199.07
1036.18
1009.96
744.24
788.85
616.04
3469.86
2360.12
1577.25
1445.88
1392.47
1265.79
537.07
BTA 0.25M + KEX 0.1M/EtOH Corr. Cu
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

FTIR Spectra: BTA + KI

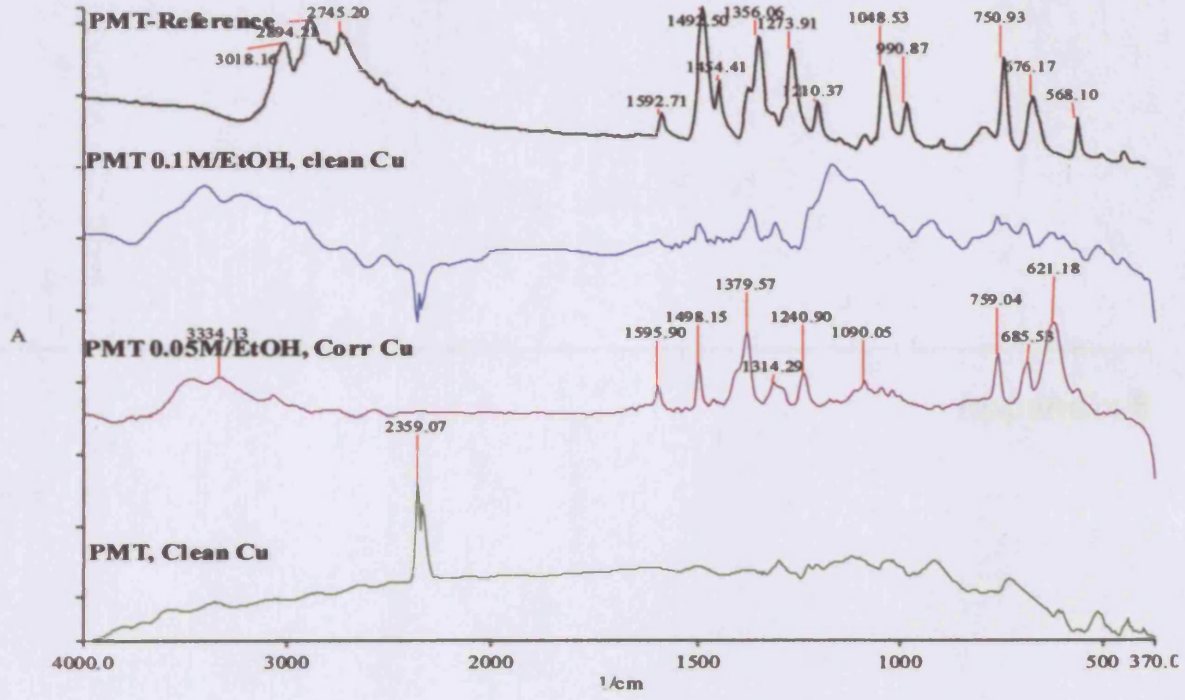


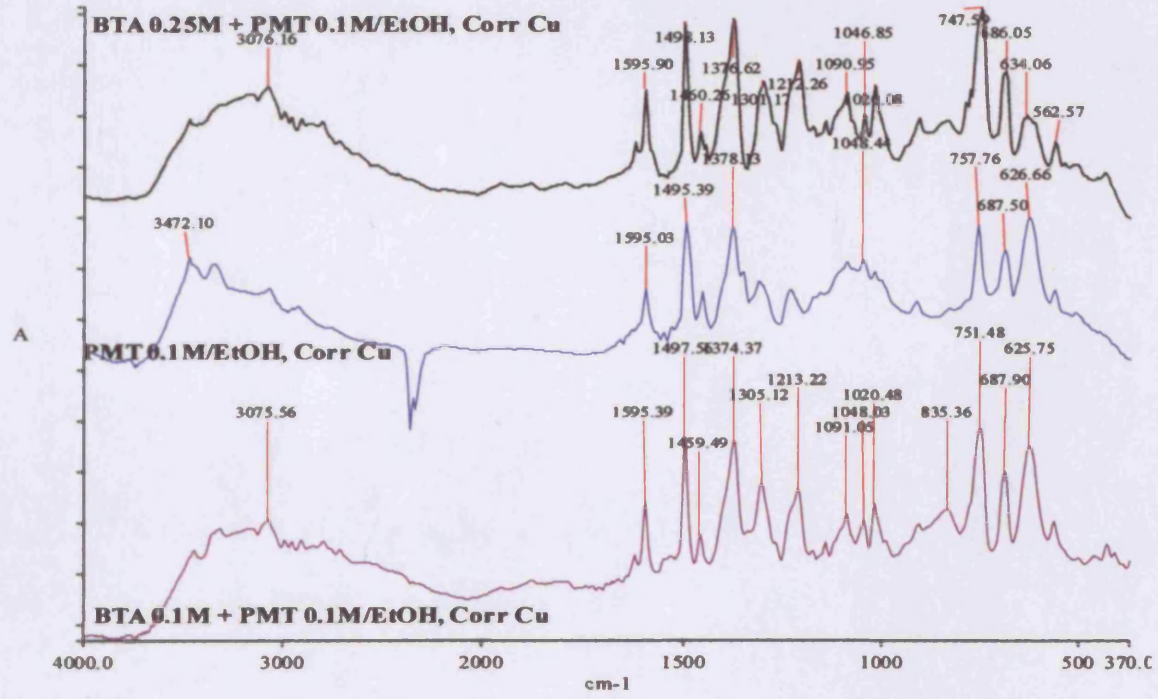



BTA 0.01M + KI 0.01M/H2O, corroded Cu
3459.34
3372.48
1651.18
1445.91
1279.28
990.04
926.68
599.69
519.01
BTA 0.25M + KI 0.1M, 1h, Corroded Cu
744.03
3269.61
3447.13
1212.22
788.77
1267.64
1026.92
925.27
1446.07
1595.33
1090.69
892.55
1392.47
1489.68
847.28
642.60
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1


BTA 0.1M + KI 0.01M/H2O, Corr Cu
3448.23
3358.97
924.25
989.19
864.90
744.92
789.60
624.98
616.93
455.33
1211.38
1446.00
1651.69
1270.17
2358.62
743.35
BTA 0.1M + KI 0.01M/EtOH, clean Cu
1152.88
1268.14
1446.01
2924.78
2359.19
787.88
A
4000.0
3000
2000
1500
1000
500
370.0
cm-1

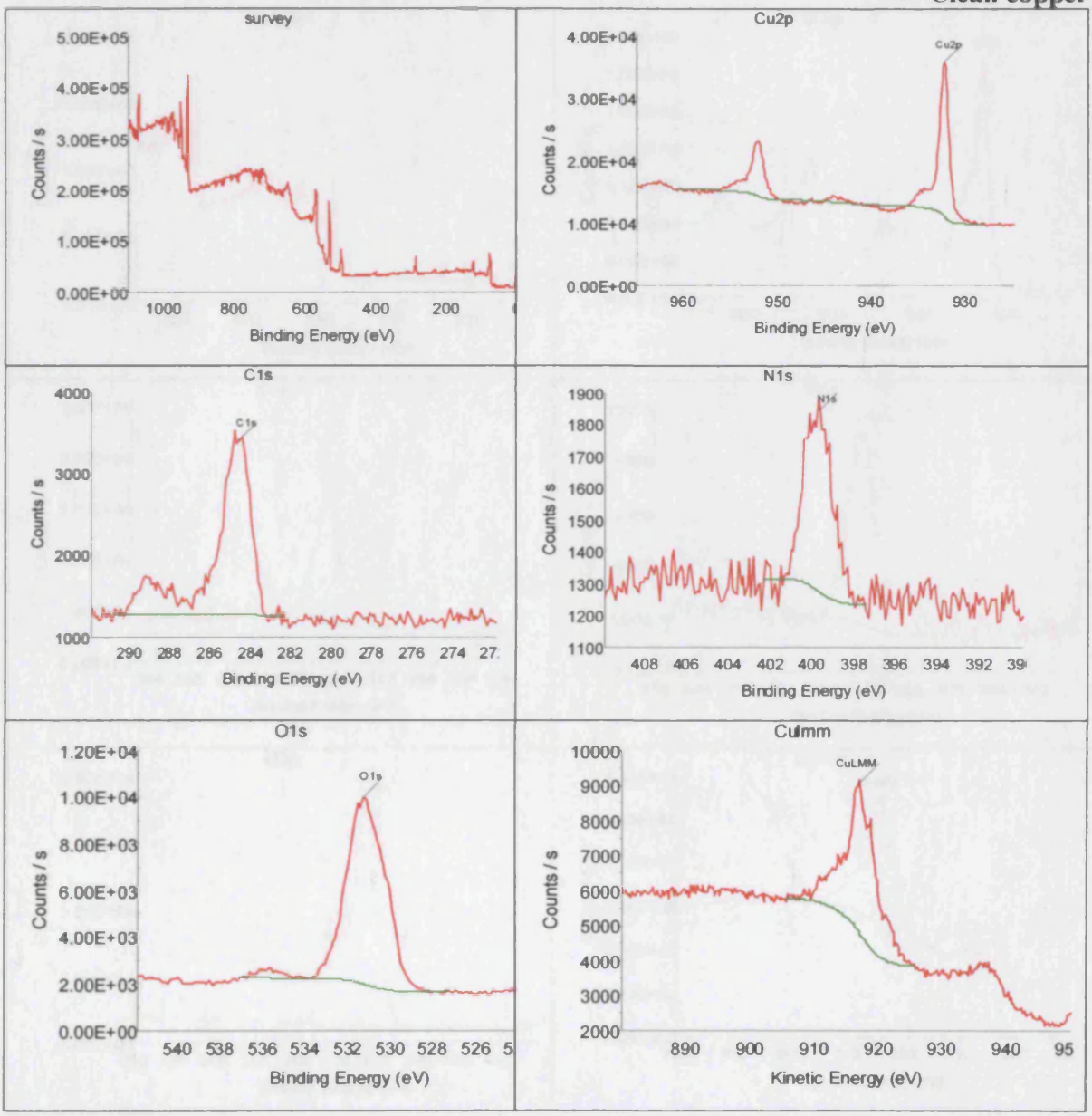
FTIR Spectra: BTA + PMT





Appendix 6

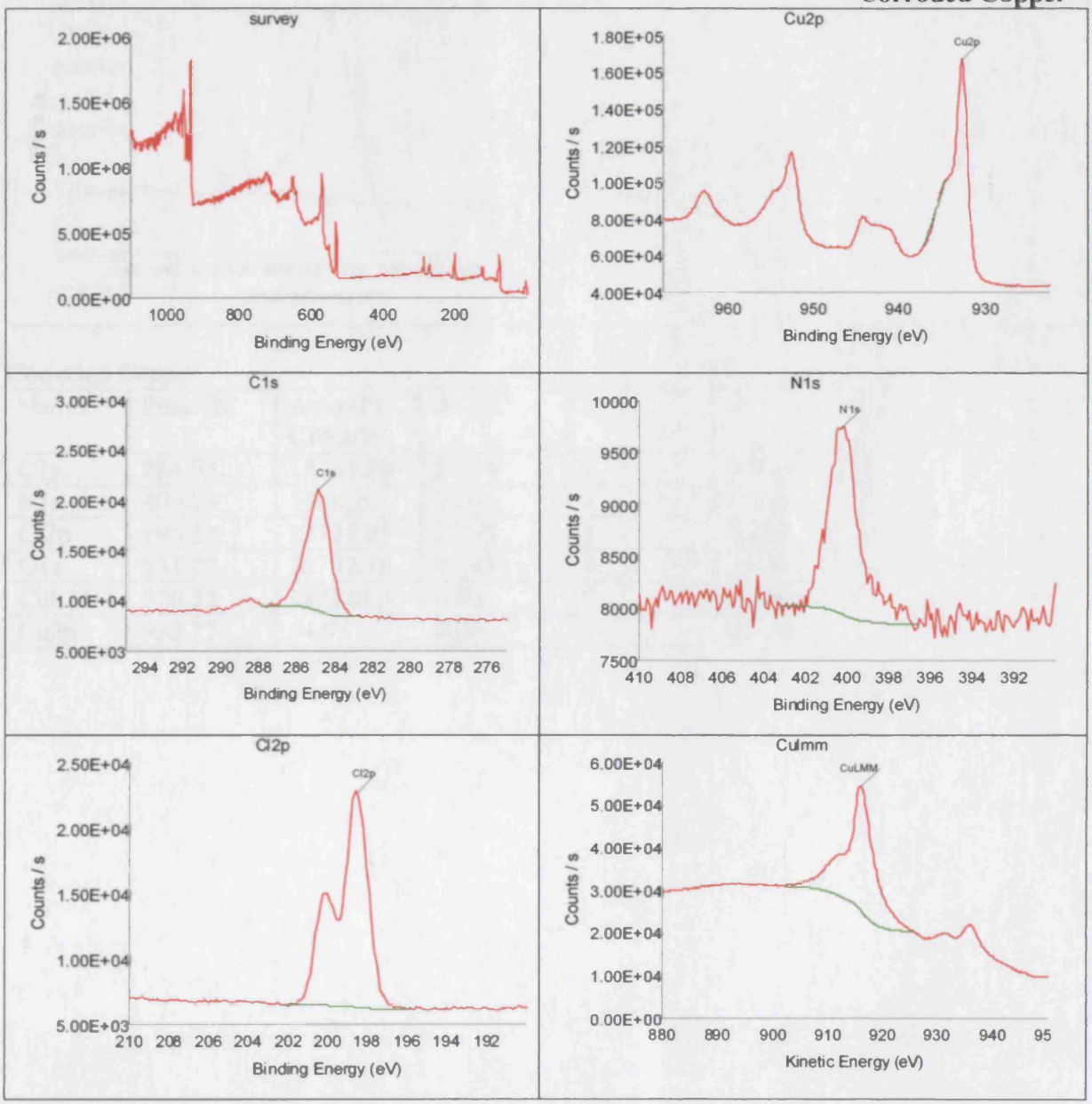
Clean copper

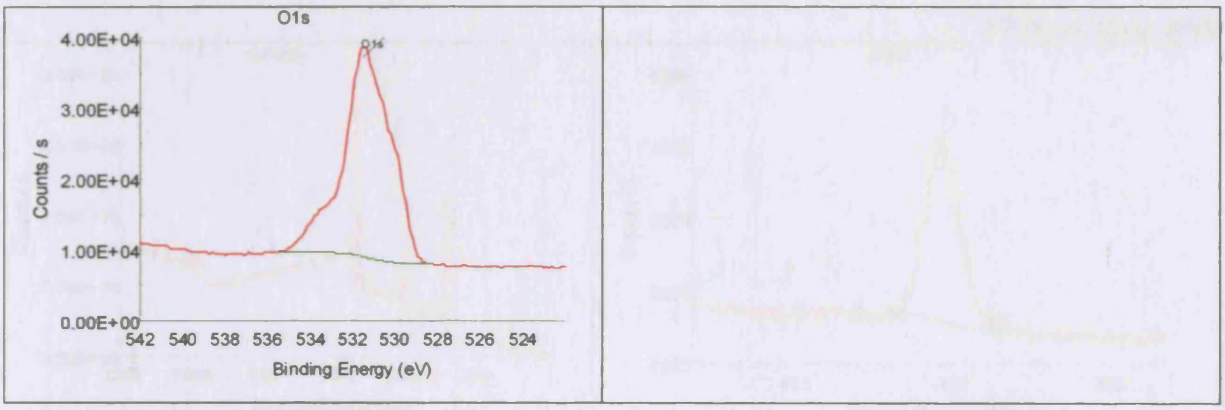


Clean copper
(Nitrogen is due to contamination of the sample).

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.60	4587.69	11.02	1	1.000
N1s	399.65	956.82	1.31	1	1.800
O1s	531.23	18166.92	15.88	1	2.930
Cu2p	932.27	52577.73	6.33	1	25.390
CuLMM	569.67	25243.55	65.45	1	1.000

Corroded Copper

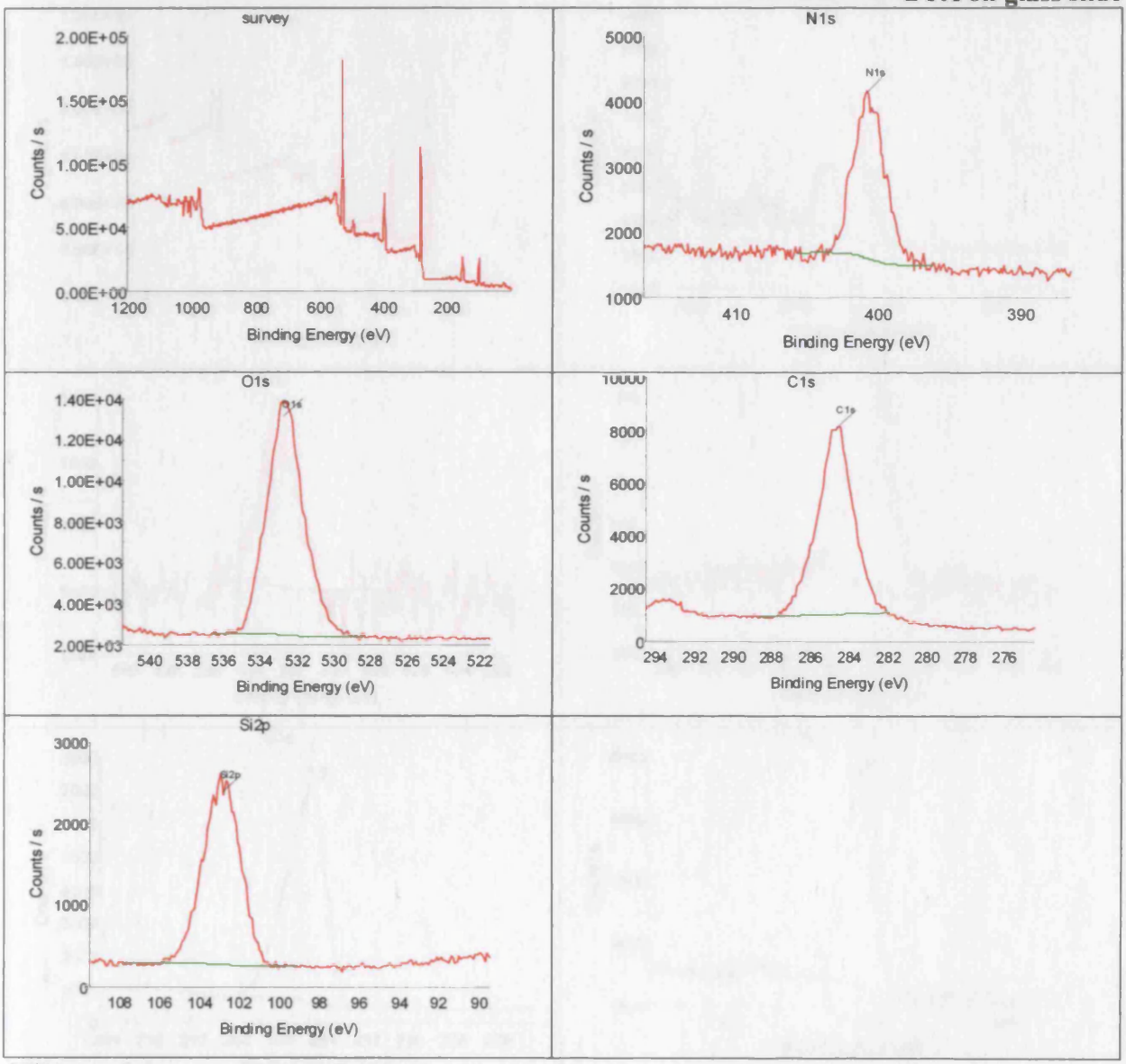




Corroded Copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.93	18363.30	29.14	1	1.000
N1s	400.24	3368.20	3.05	1	1.800
Cl2p	198.52	32735.05	22.33	1	2.285
O1s	531.47	78752.18	45.47	1	2.930
CuLMM	570.52	184848.33	0.00	0	1.000
Cu2p	932.77	54.97	0.00	1	25.390

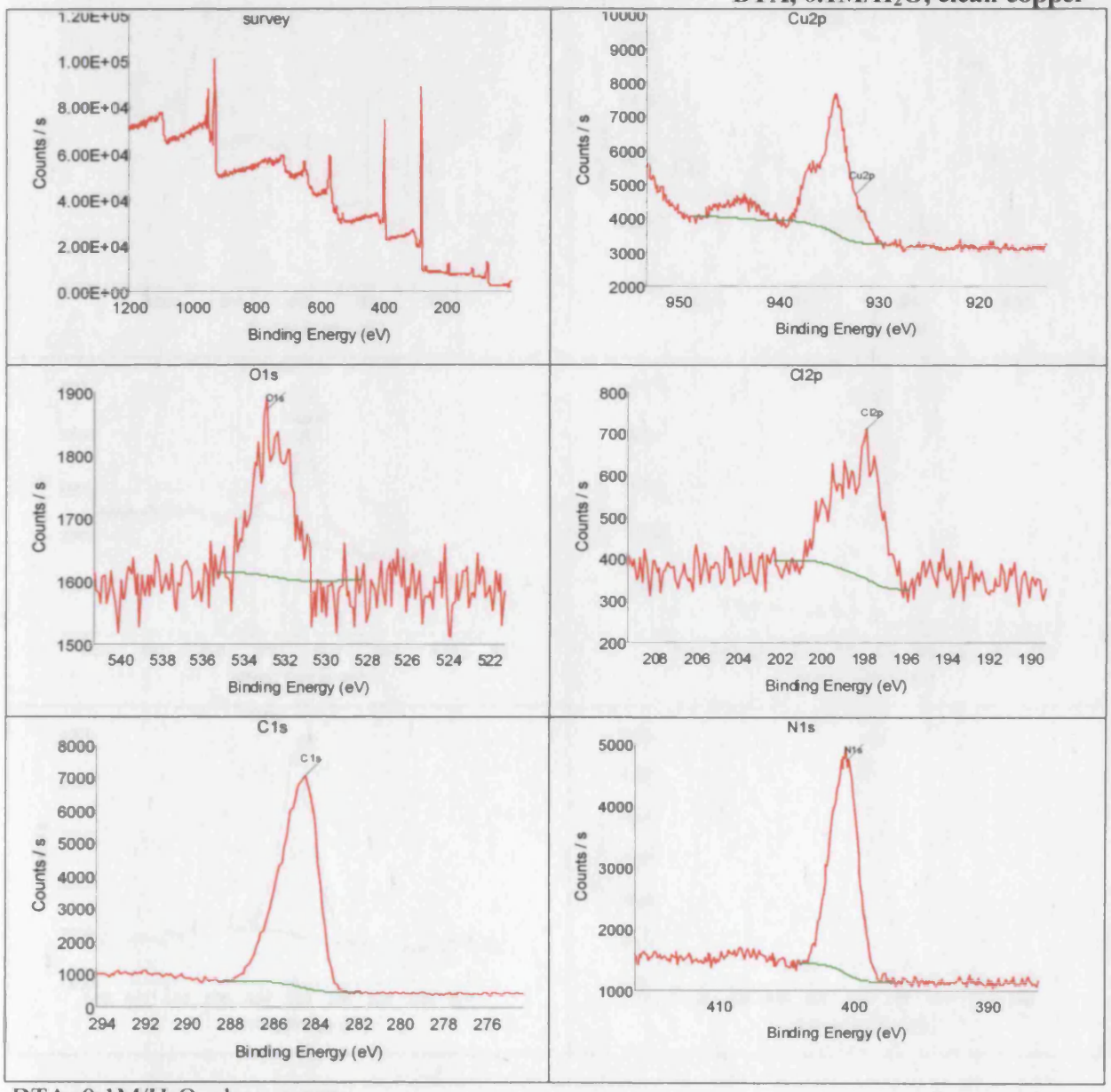
BTA on glass slide



BTA on glass

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.68	15766.84	44.35	1	1
Cl2p	199.53	204.71	0.25	1	2.285
N1s	400.81	6591.81	10.59	1	1.8
O1s	532.72	27278.53	27.93	1	2.93
Si2p	102.81	5078.07	16.88	1	0.817

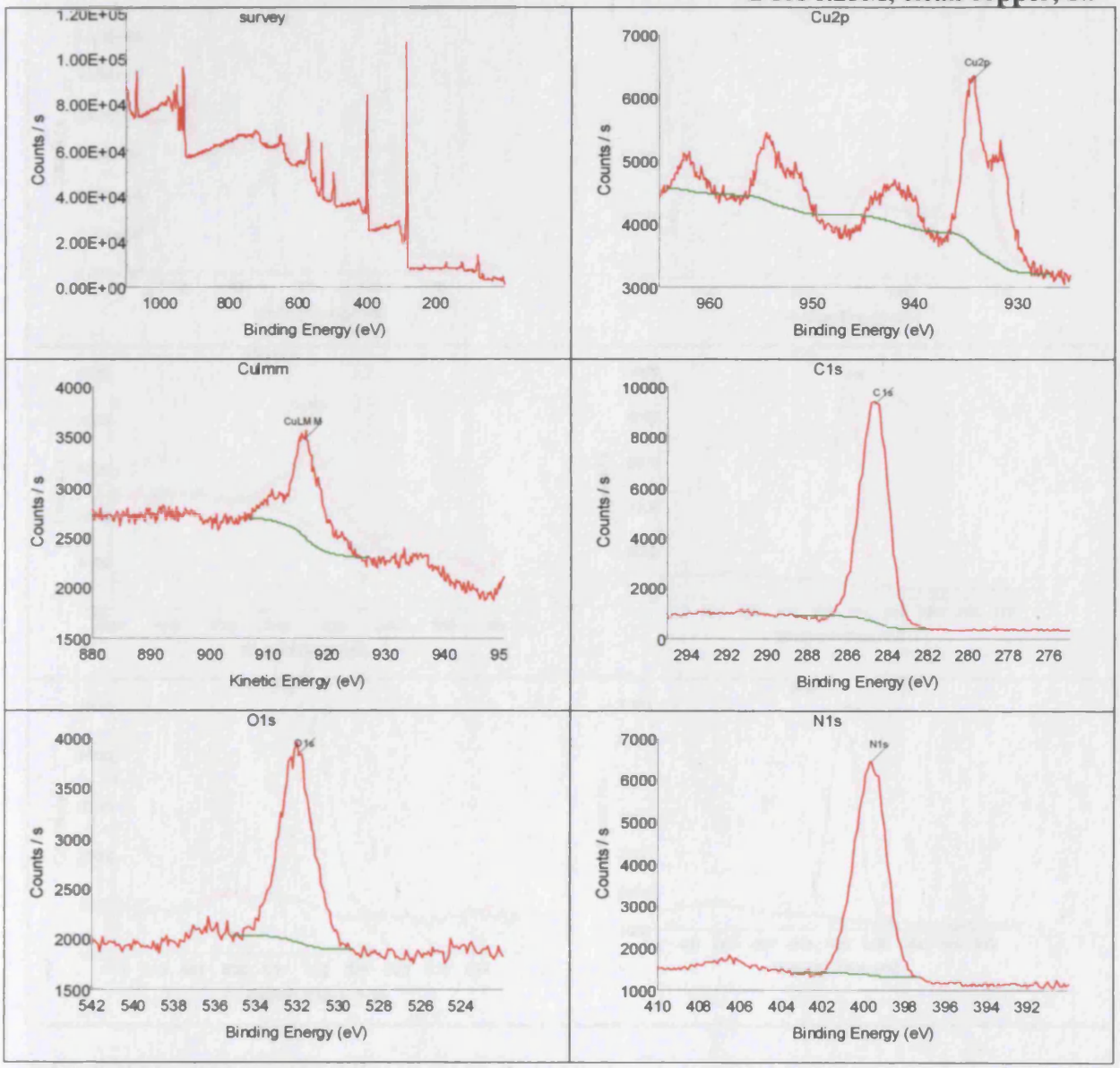
BTA, 0.1M/H_2O, clean copper



BTA, 0.1M/H_2O, clean copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.6	13886.2	66.7	1.0	1.0
Cl2p	197.9	844.7	1.7	1.0	2.3
Cu2p	934.3	349320.5	6.7	1.0	25.4
CuLMM	571.8	249488.5	0.0	0.0	1.0
N1s	400.6	8622.4	23.7	1.0	1.8
O1s	532.9	668.2	1.2	1.0	2.9

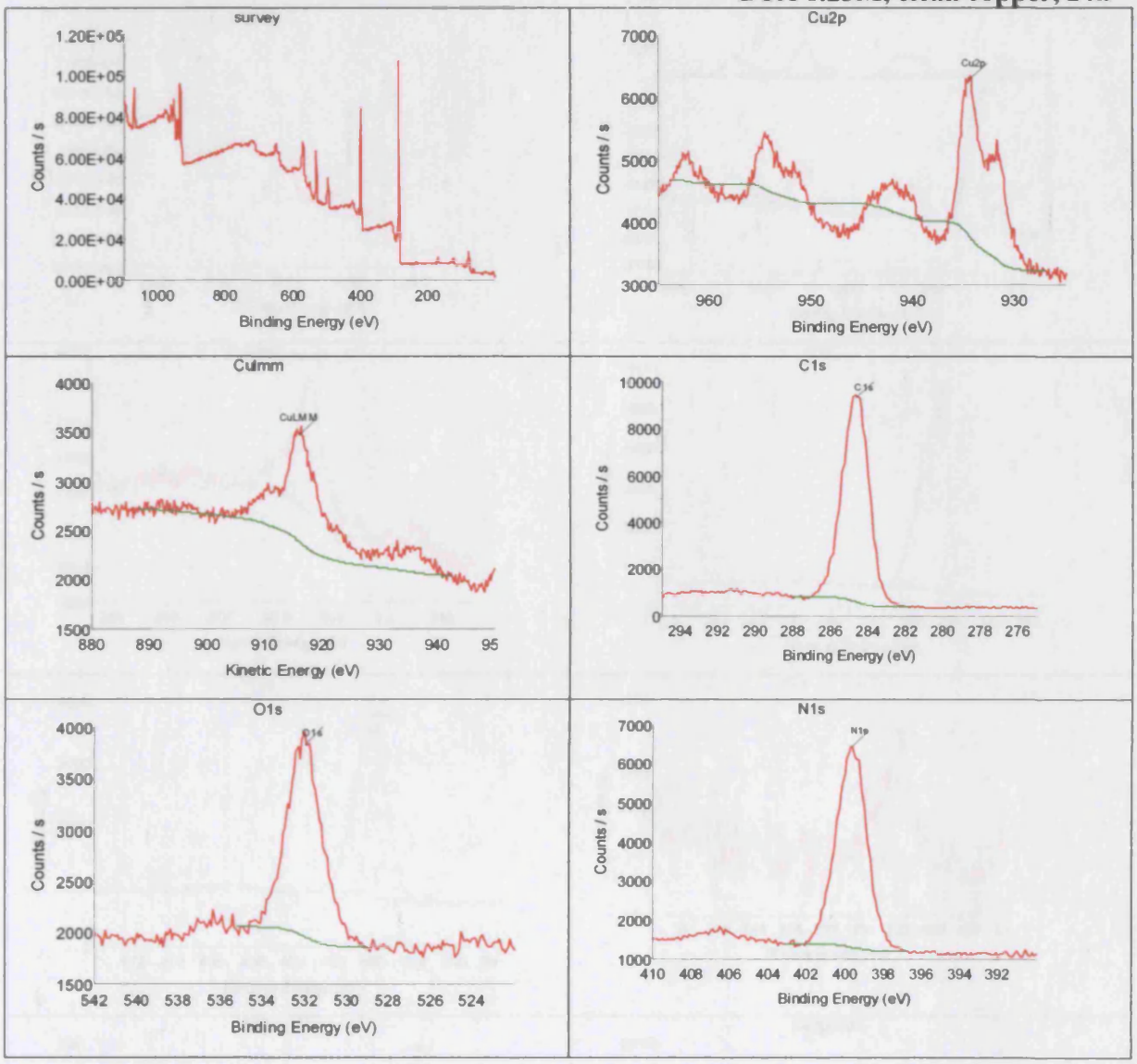
BTA 0.25M, clean copper, 1h



BTA 0.25M, clean copper, 1h

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.65	15012.28	65.99	1	1.000
N1s	399.63	9627.40	24.16	1	1.800
Cl2p	199.76	-0.51	0.00	0	2.285
O1s	531.97	3917.51	6.27	1	2.930
CuLMM	570.42	6766.87	0.00	0	1.000
Cu2p	934.49	16262.01	3.59	1	25.390

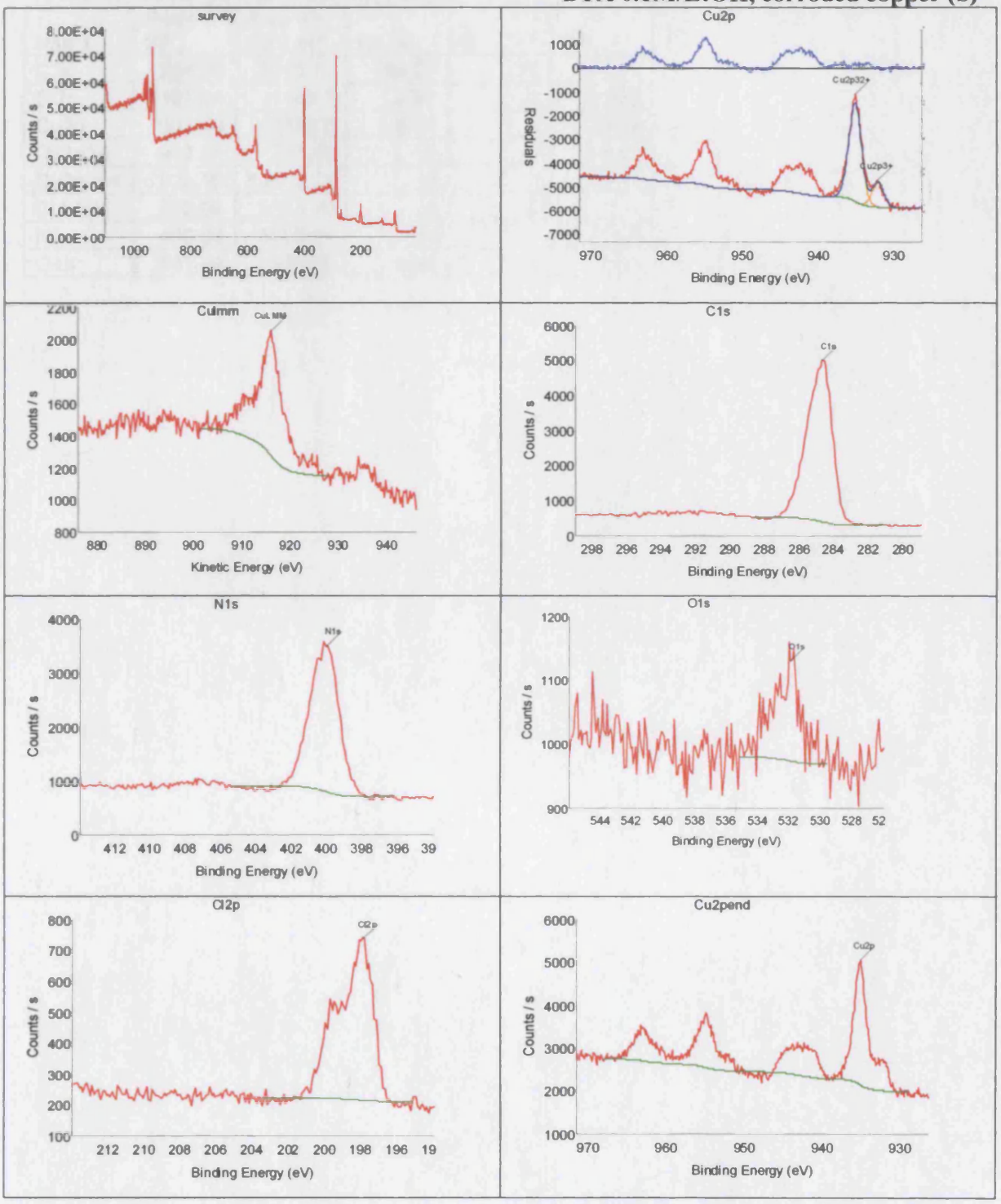
BTA 0.25M, clean copper, 24h



BTA 0.25M, clean copper, 24h

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.66	15378.03	66.69	1	1
Cu2p	934.44	11376.27	2.47	1	25.39
CuLMM	570.43	11913.99	0	0	1
N1s	399.63	9937.86	24.6	1	1.8
O1s	531.96	3952.72	6.24	1	2.93

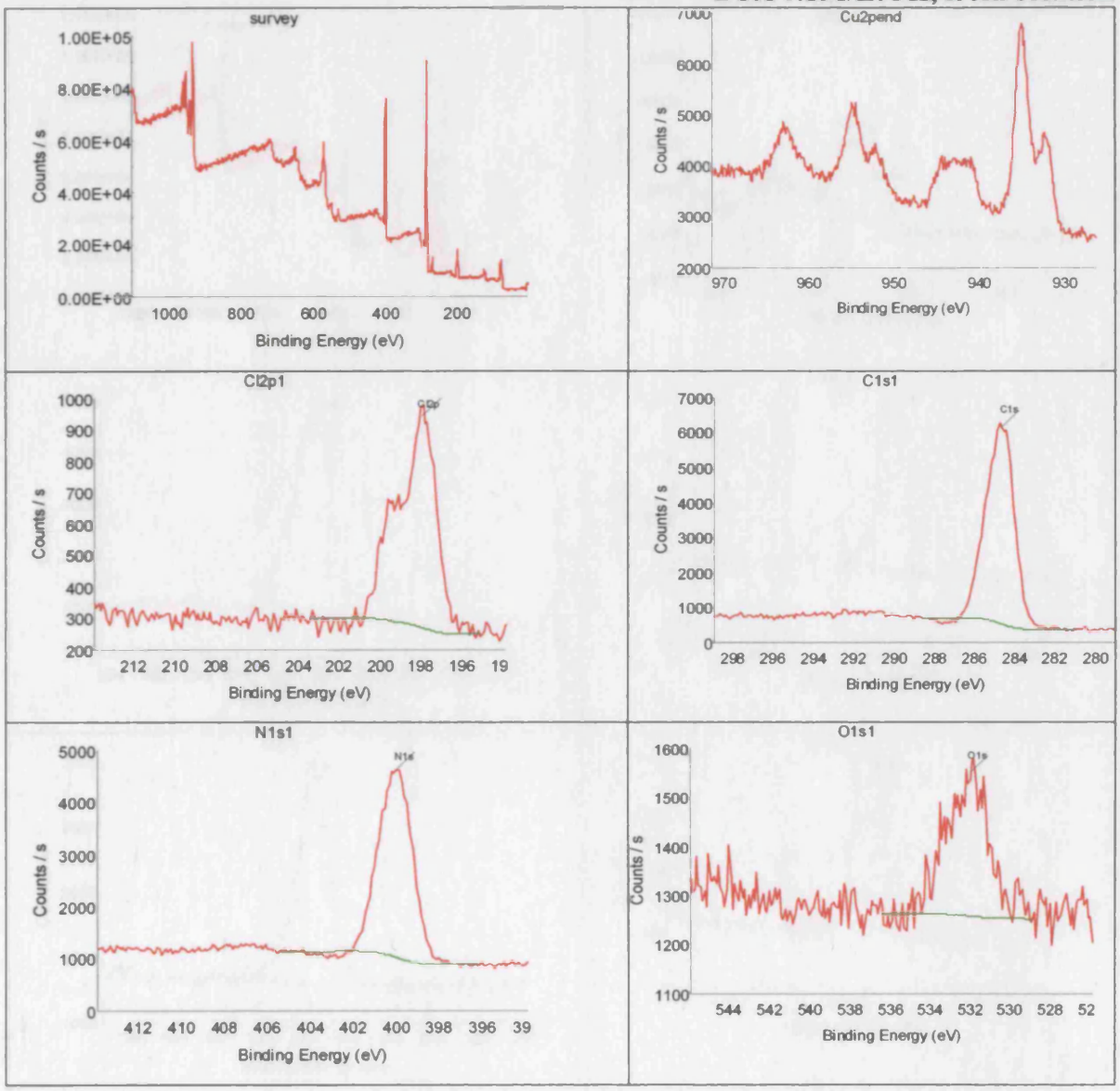
BTA 0.1M/EtOH, corroded copper (b)



BTA 0.1M/EtOH, corroded copper (b)

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.66	8116.71	64.27	1	1
Cl2p	197.94	1165.3	3.97	1	2.285
Cu2p	935.18	17160.5	6.82	1	25.39
Cu2p3+	932.21	237.46	0	0	16.73
Cu2p32+	935.16	12602.71	0	0	16.73
CuLMM	570.69	5368.86	0	0	1
N1s	400.03	5309.01	24	1	1.8
O1s	531.86	329.58	0.95	1	2.93

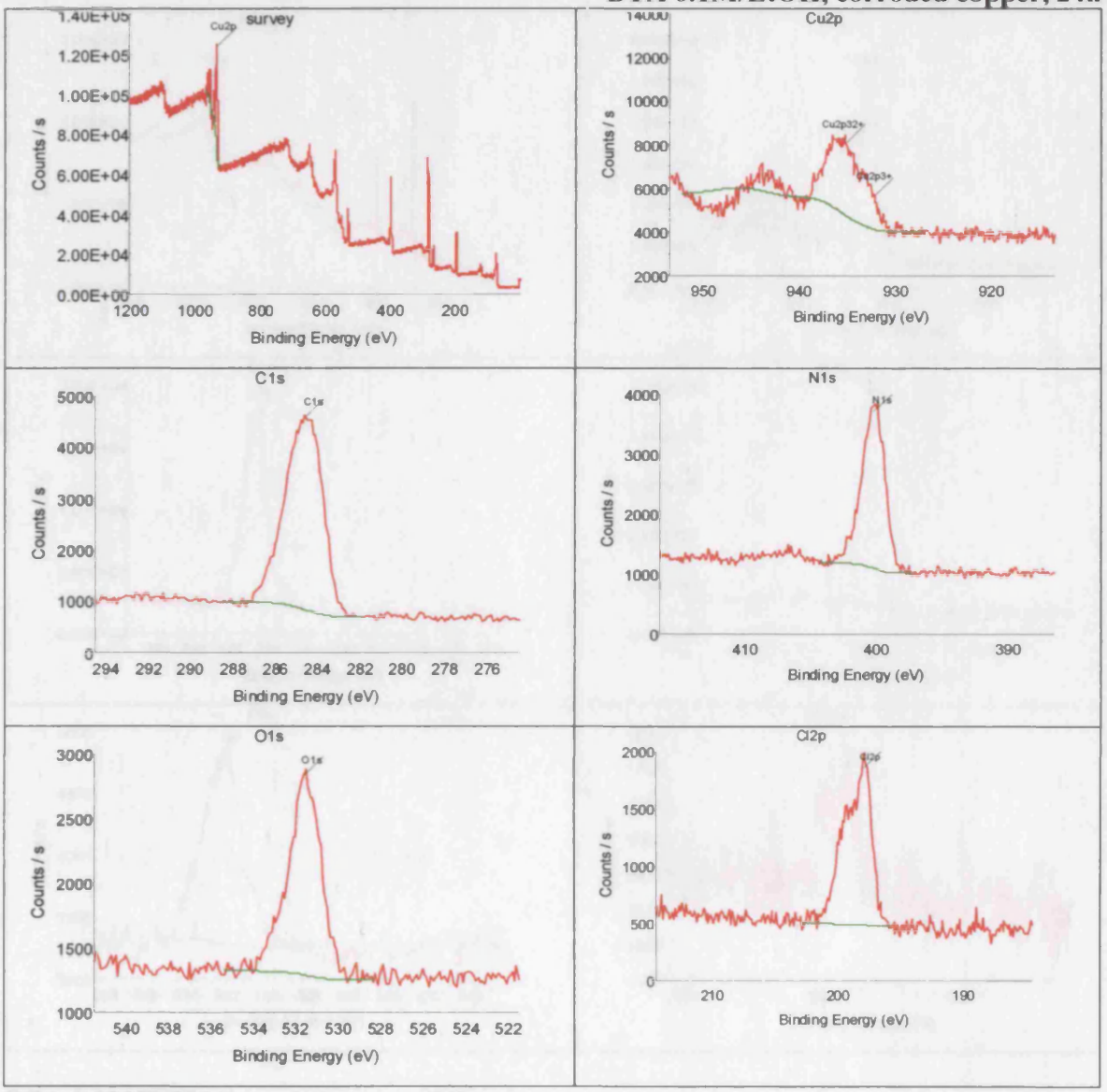
BTA 0.1M/EtOH, fresh solution



BTA 0.1M/EtOH, fresh solution

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.6	9533.2	61.9	1.0	1
Cl2p	197.9	1512.6	4.2	1.0	2.285
Cu2p	935.0	22180.3	7.2	1.0	25.39
Cu2p3+	932.3	3811.4	0.0	0.0	16.73
Cu2p32+	935.0	5861.0	0.0	0.0	16.73
CuLMM	570.6	11469.4	0.0	0.0	1
N1s	400.0	6735.5	24.9	1.0	1.8
O1s	532.0	750.1	1.8	1.0	2.93

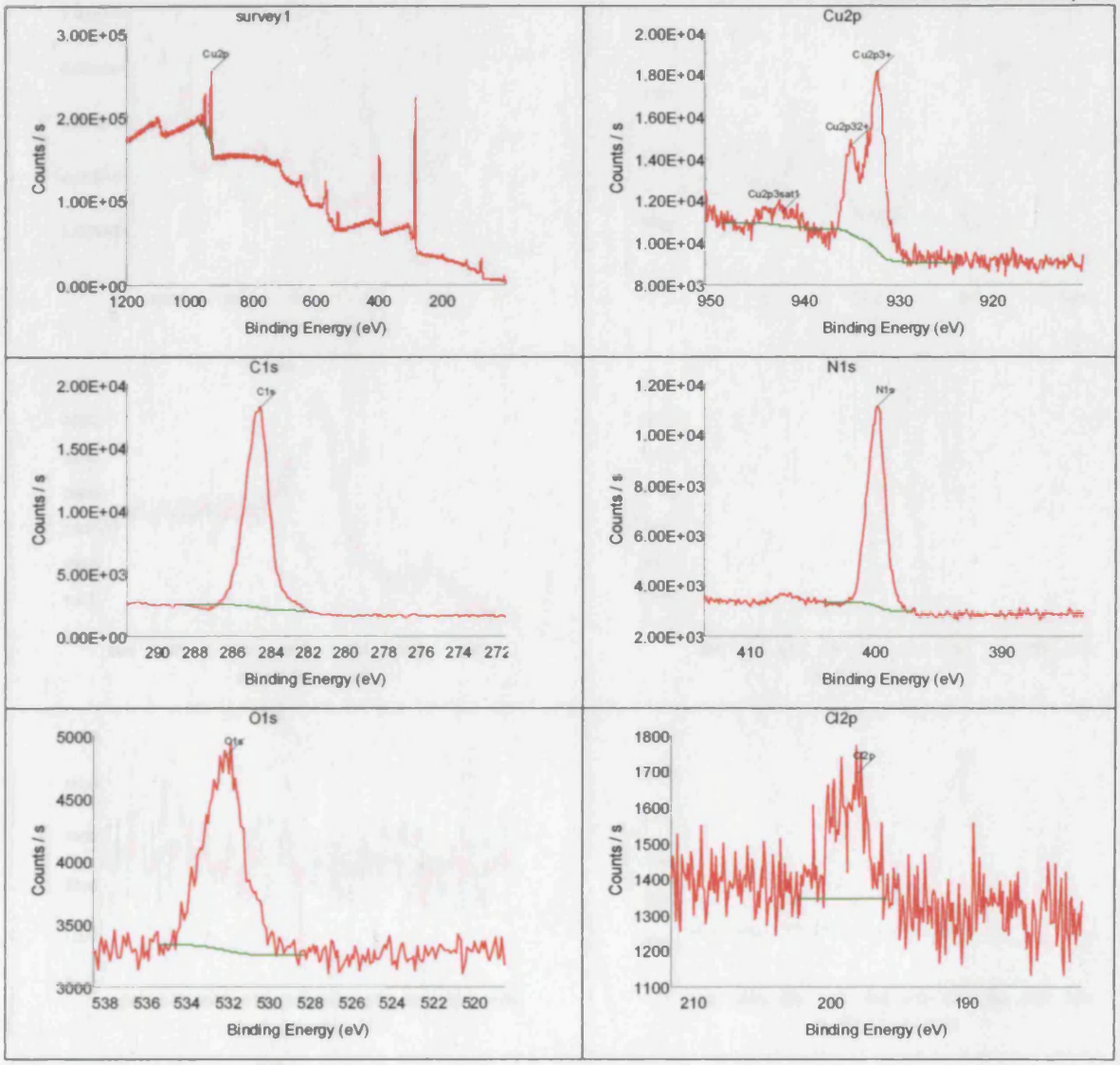
BTA 0.1M/EtOH, corroded copper, 24h



BTA 0.1M/EtOH, corroded copper, 24h

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.6	8049.2	50.6	1.0	1.0
Cl2p	197.9	3738.5	10.1	1.0	2.3
Cu2p	935.0	441489.7	11.1	1.0	25.4
N1s	400.1	5968.7	21.4	1.0	1.8
O1s	531.6	2963.8	6.8	1.0	2.9

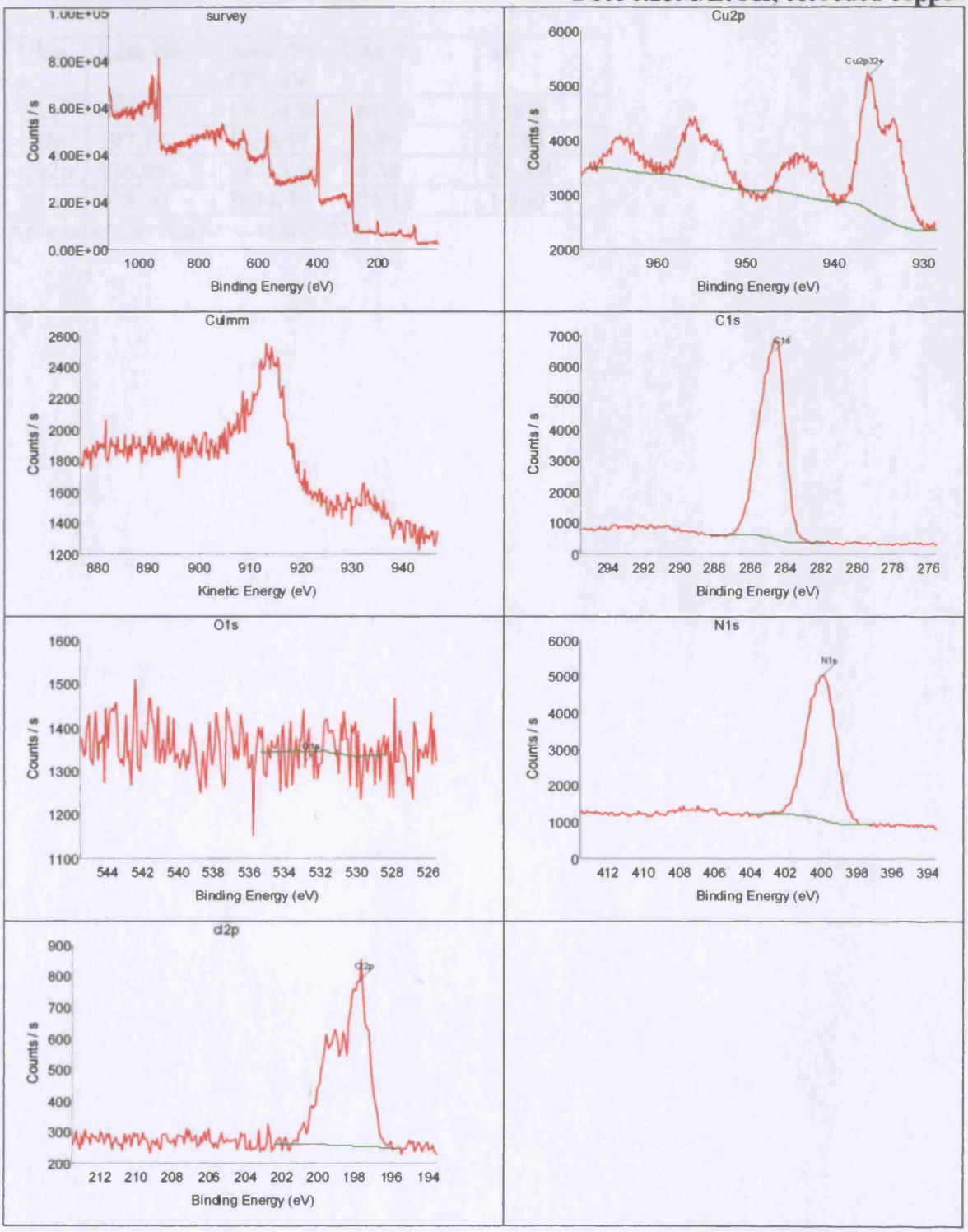
BTA 0.1M/H2O, 1h



BTA 0.1M/H2O, 1h

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.66	24599.04	66.41	1	1
Cl2p	198.04	1020.79	1.18	1	2.285
Cu2p	932.49	698170.4	7.54	1	25.39
N1s	399.88	13756.26	21.2	1	1.8
O1s	532.11	3731.84	3.67	1	2.93

BTA 0.25M/EtOH, corroded copper

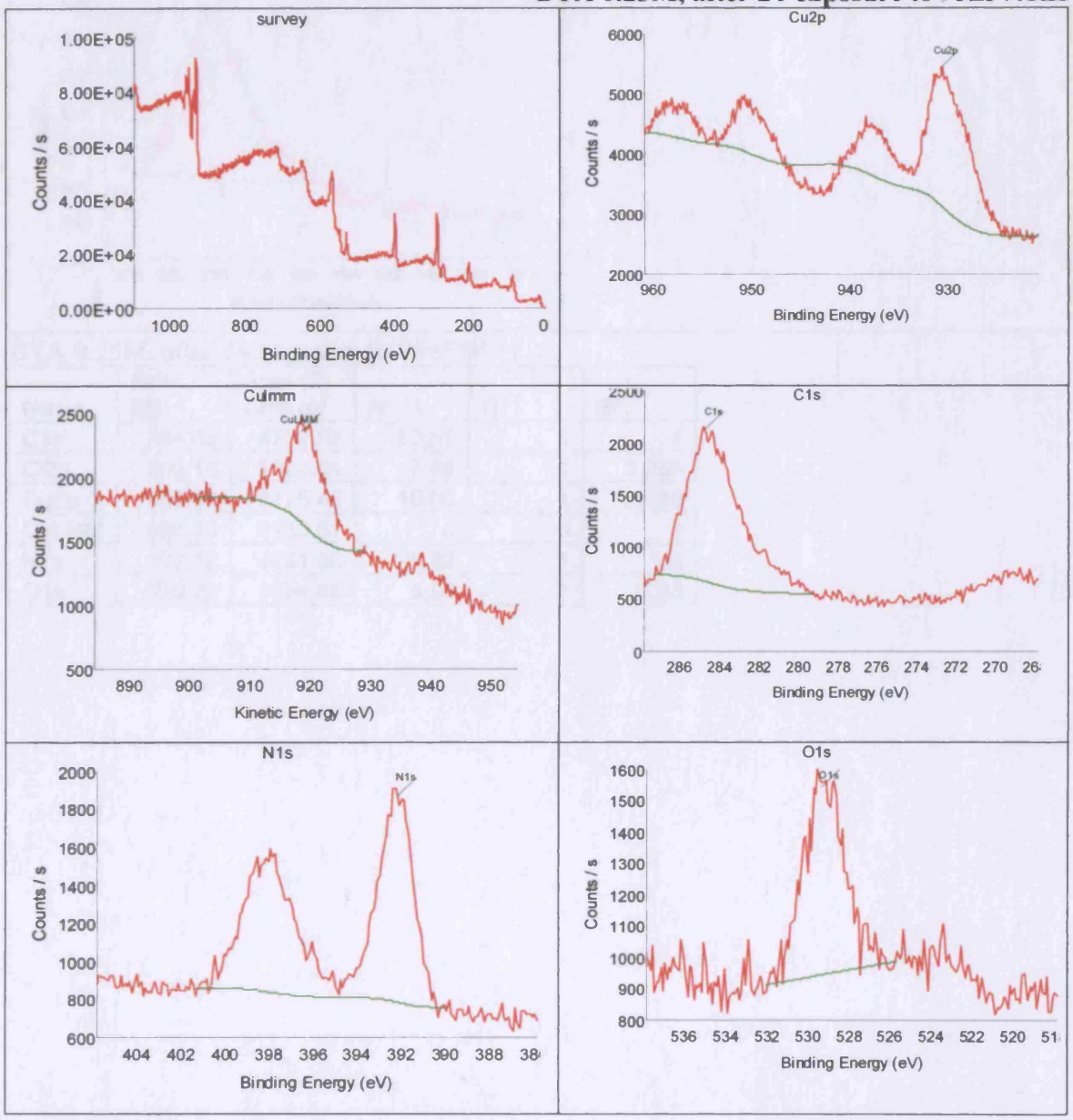


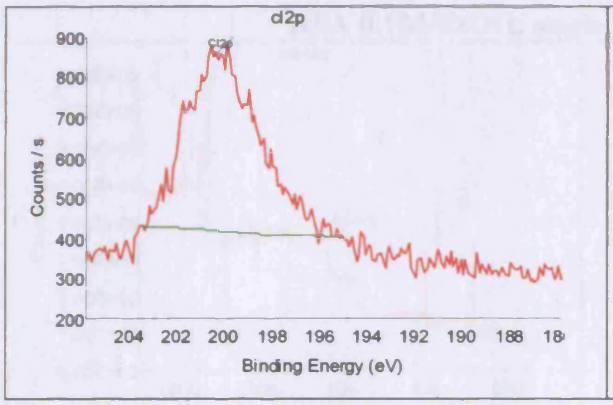
BTA 0.25M/EtOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	SF
C1s	284.61	11024.98	64.36	1.000
Cl2p	197.79	1258.97	3.16	2.285
Cu2p	936.09	21755.94	6.38	25.390
N1s	399.90	7834.49	26.11	1.800

Area ratio Cu+:Cu++ = 4580/6224

BTA 0.25M, after 24-exposure to 95±5%RH

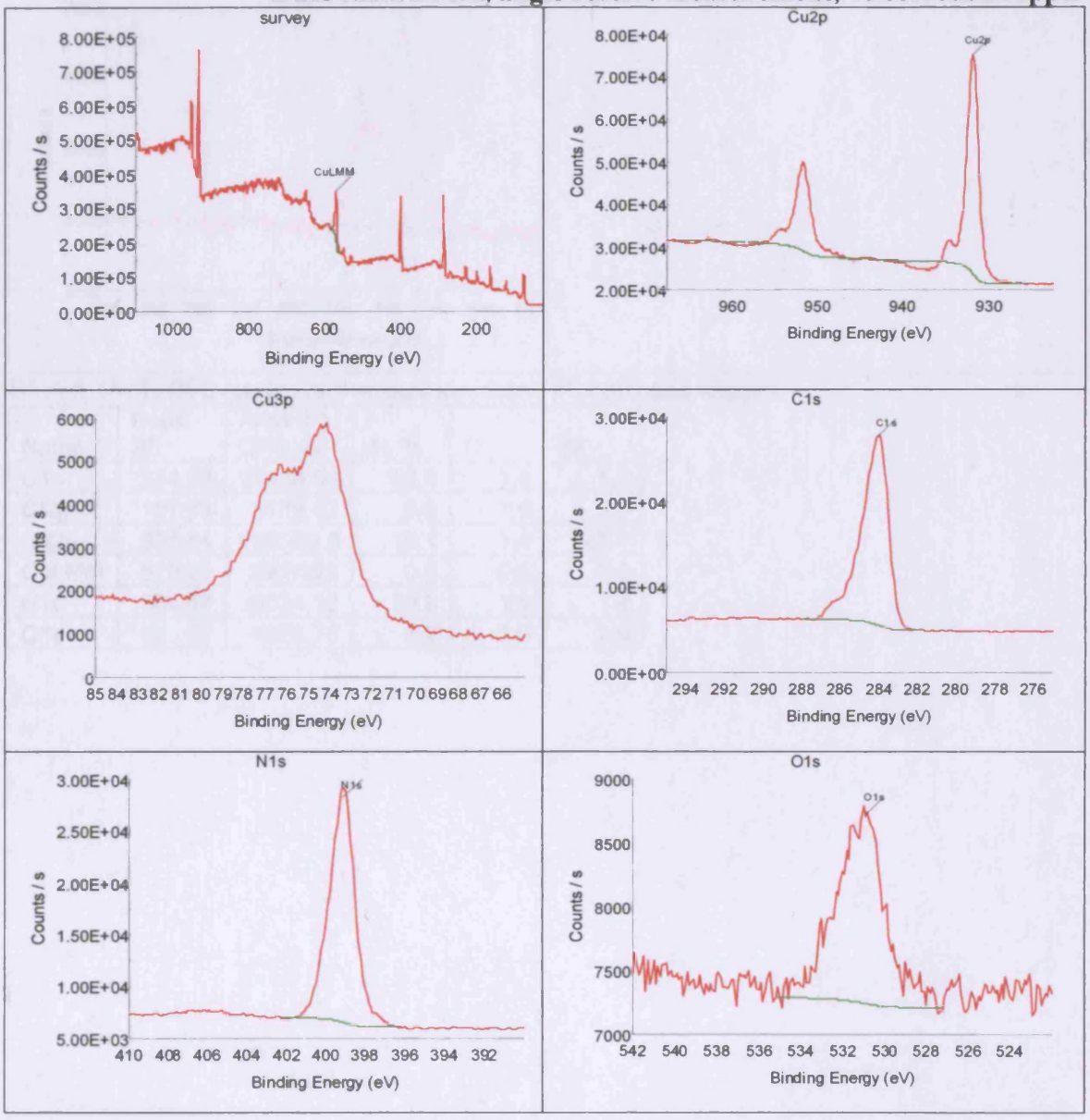


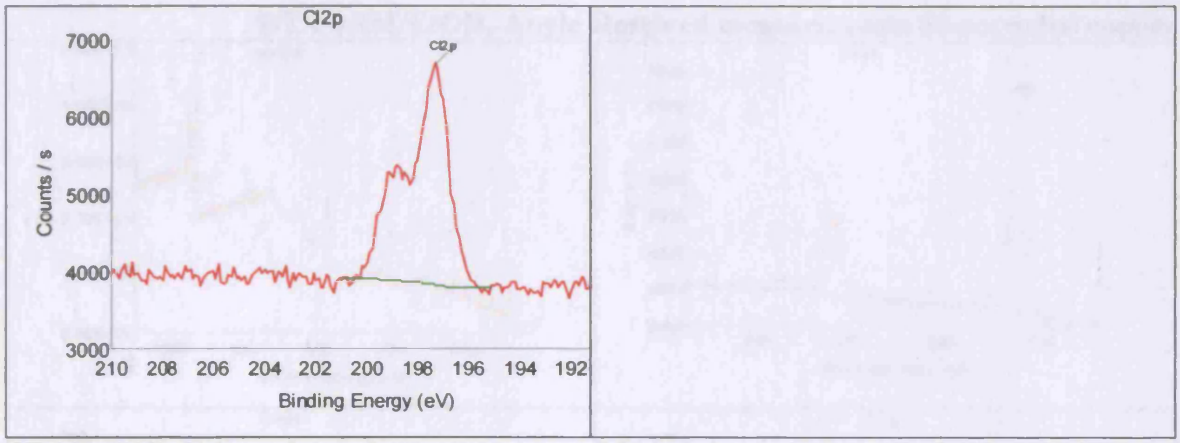


BTA 0.25M, after 24-exposure to 95±5%RH

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.65	4732.82	50.69	1	1
Cl2p	200.16	1624.84	7.48	1	2.285
Cu2p	930.51	18778.45	10.06	1	25.39
CuLMM	568.19	6133.81	0	0	1
N1s	392.12	4231.86	25.82	1	1.8
O1s	529.39	1524.48	5.94	1	2.93

BTA 0.1M/EtOH, angle resolve measurement, 00 corroded copper

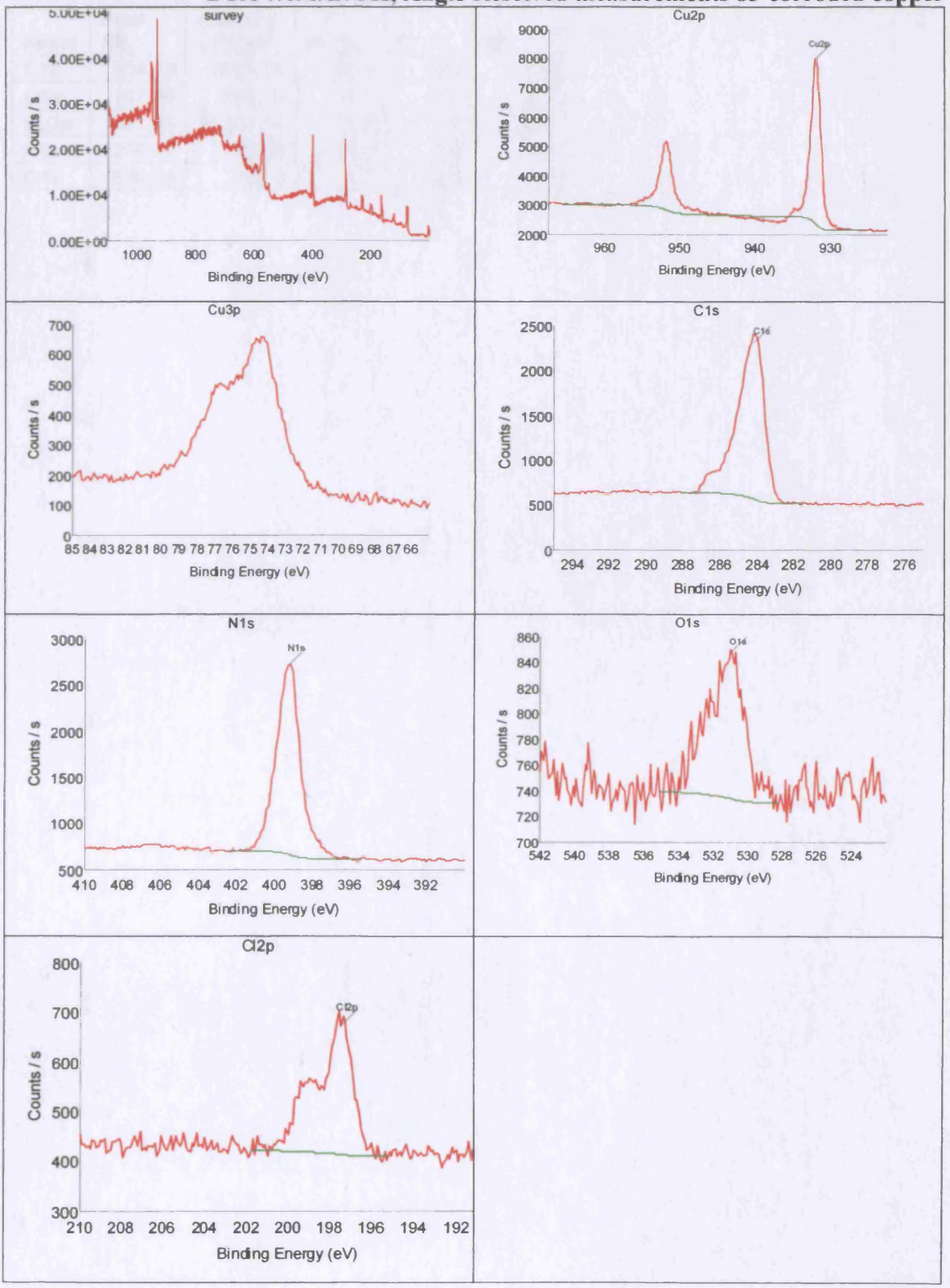




BTA 0.1M/EtOH, angle resolve measurement, 00 corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.03	37434.61	54.3	1.0	1.0
Cl2p	197.33	5719.62	3.6	1.0	2.3
Cu2p	931.84	138520.8	10.1	1.0	25.4
CuLMM	570.21	1009323	0.0	0.0	1.0
N1s	399.08	36034.19	29.8	1.0	1.8
O1s	530.88	4203.78	2.2	1.0	2.9

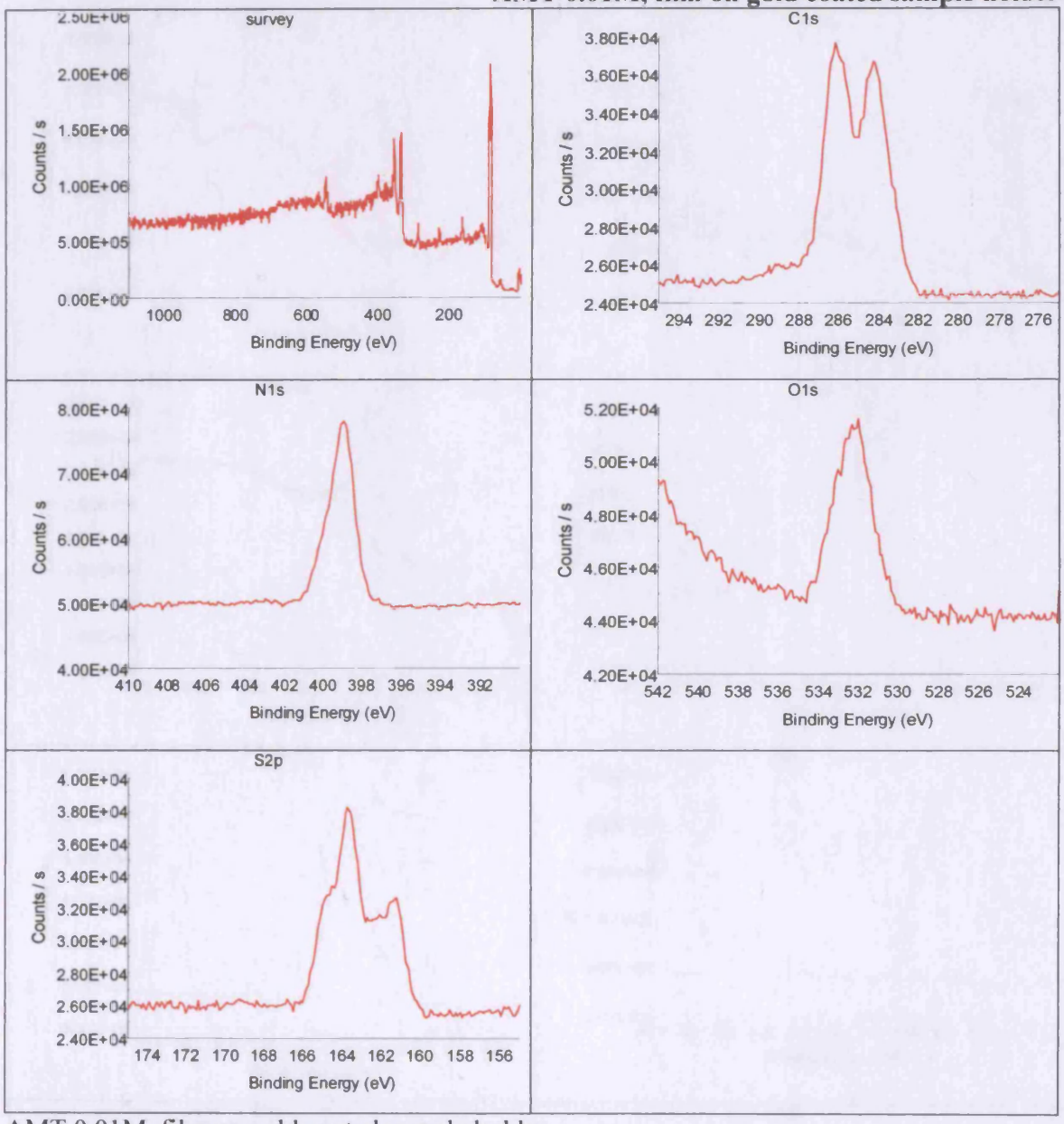
BTA 0.1M/EtOH, Angle Resolved measurements 85-corroded copper



BTA 0.1M/EtOH, Angle Resolved measurements 85-corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.13	3261.94	52.5	1.0	1.0
Cl2p	197.49	596.15	4.1	1.0	2.3
Cu2p	931.99	14760.14	11.9	1.0	25.4
N1s	399.19	3235.54	29.7	1.0	1.8
O1s	530.94	293.2	1.7	1.0	2.9

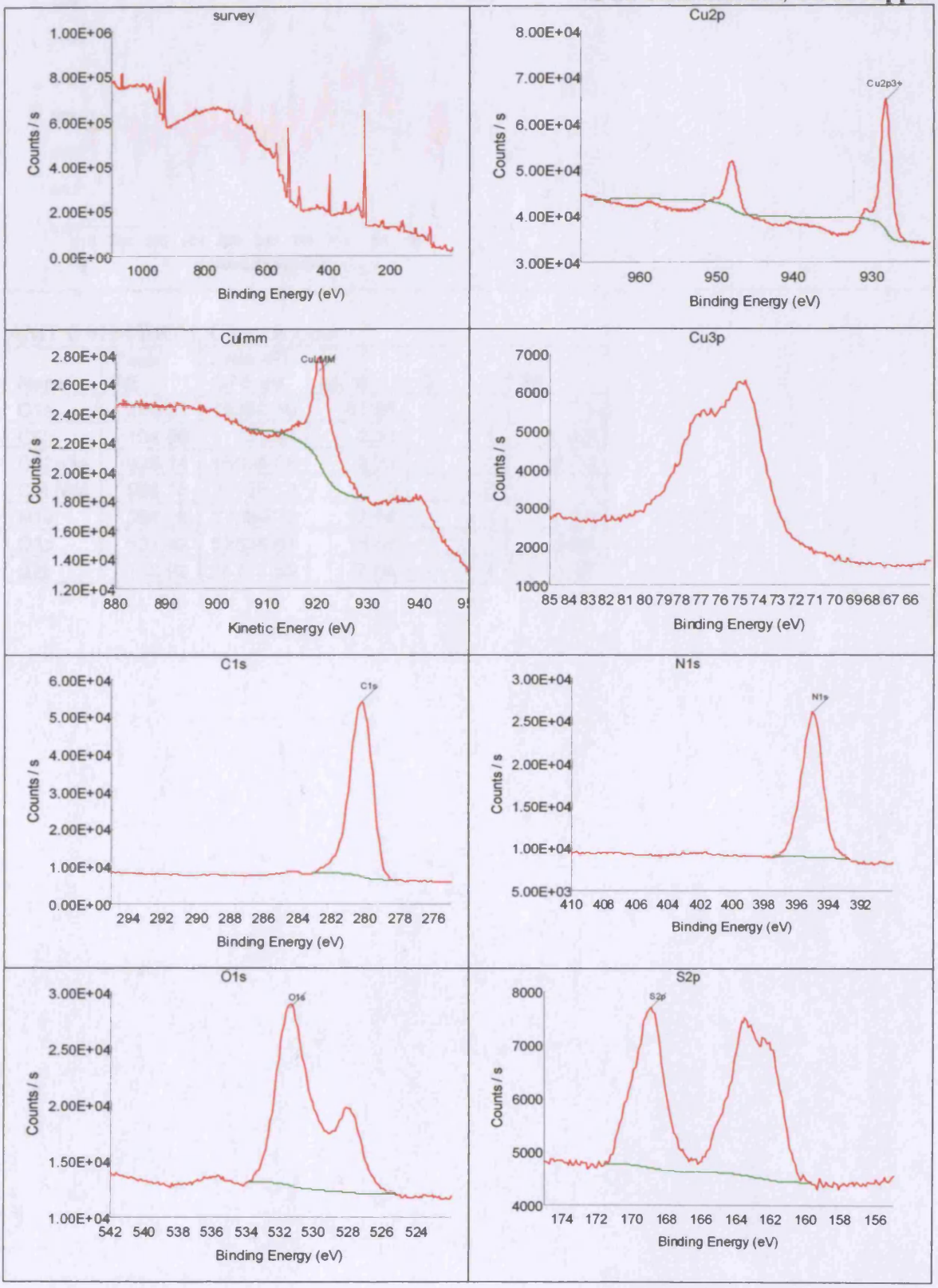
AMT 0.01M, film on gold coated sample holder

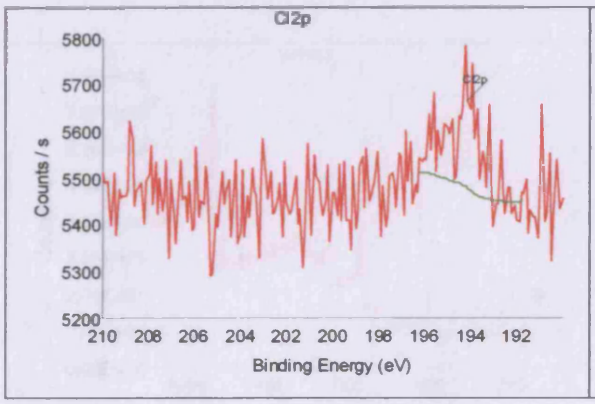


AMT 0.01M, film on gold coated sample holder

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	286.15	42853.25	44.7	1	1
N1s	398.99	46607.13	27.74	1	1.8
O1s	532.15	15693.88	5.96	1	2.93
S2p	163.66	35443.93	21.6	1	1.67

AMT 0.01M/EtOH, Clean copper

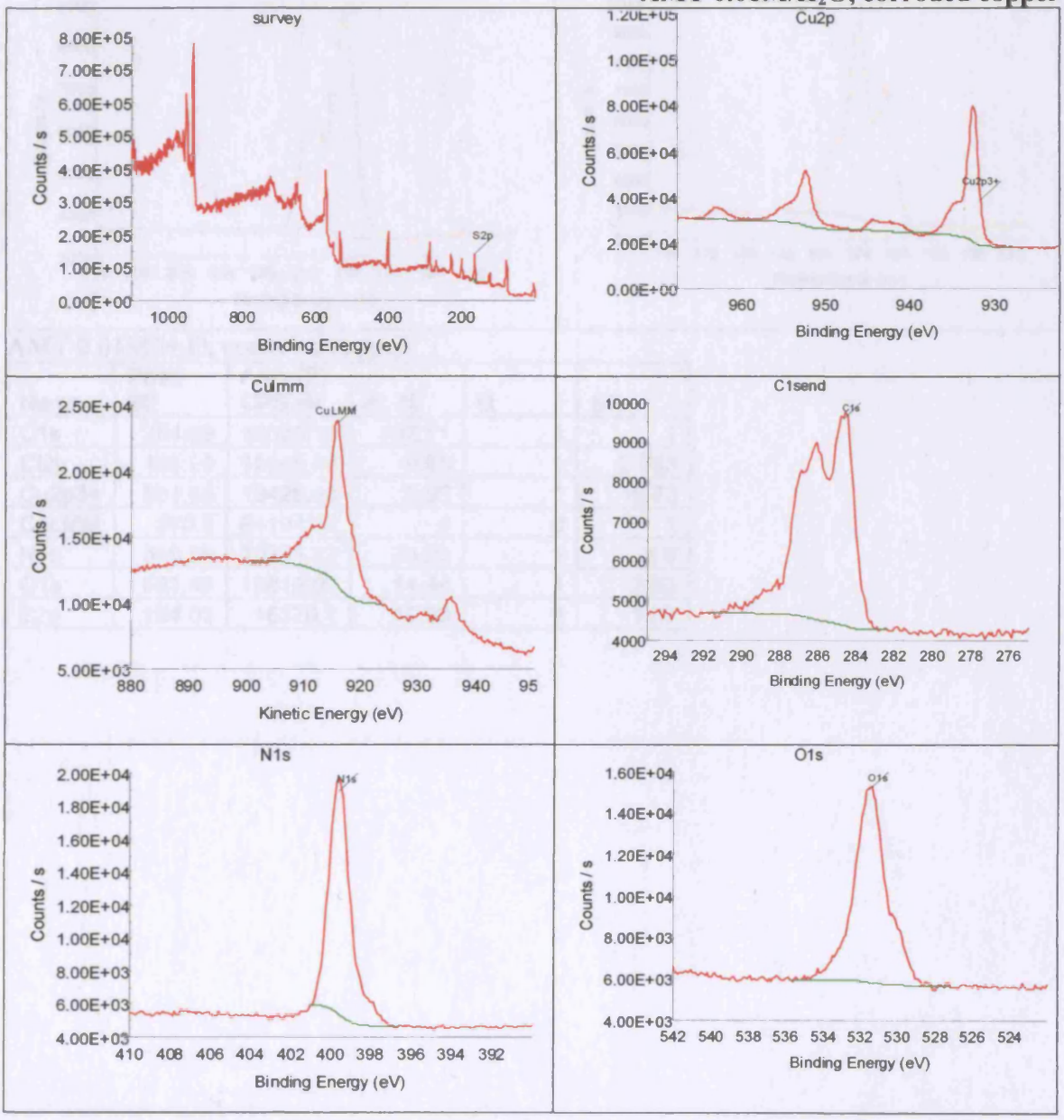


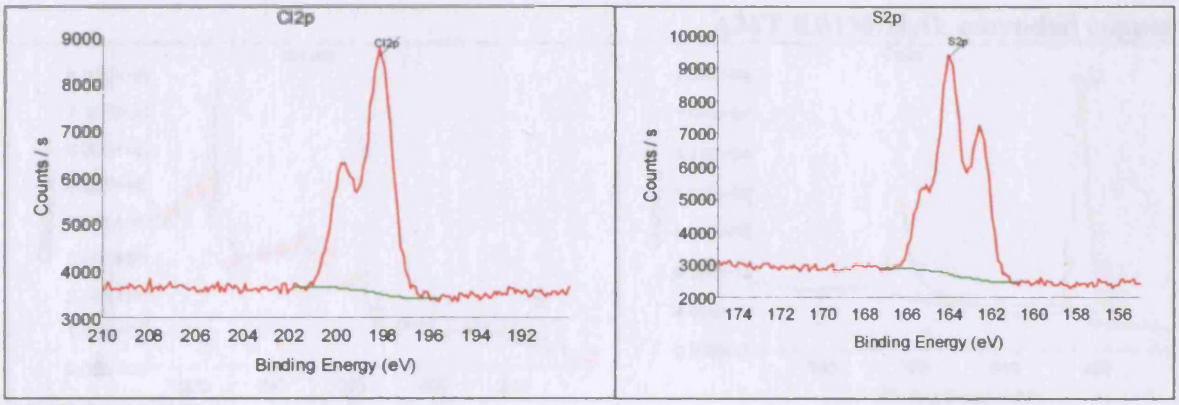


AMT 0.01M/EtOH, Clean copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	280.21	75352.49	61.26	1	1
Cl2p	194.06	335.24	0.12	1	2.285
Cu2p3+	928.14	46834.08	2.89	1	16.73
CuLMM	566.15	37139.72	0	0	1
N1s	394.98	27084.06	12.56	1	1.8
O1s	531.42	52334.61	15.49	1	2.93
S2p	168.92	16127.53	7.68	1	1.67

AMT 0.01M/H_2O, corroded copper

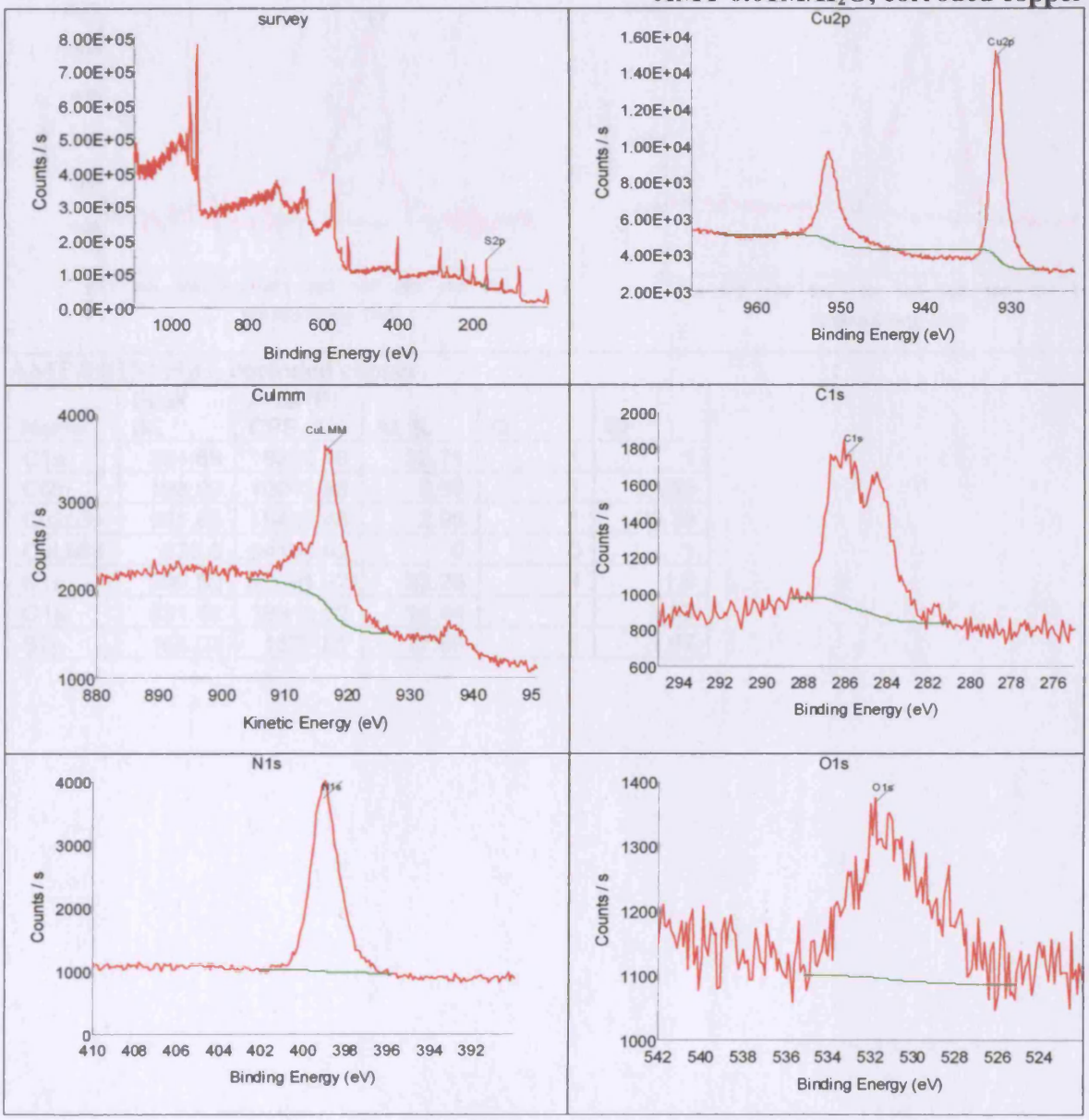


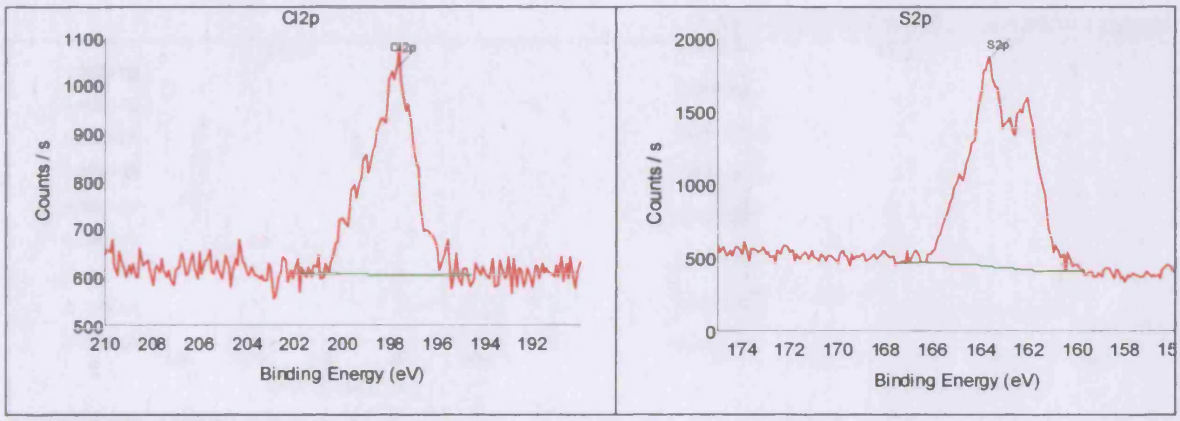


AMT 0.01M/H_2O, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.69	16328.19	32.71	1	1
Cl2p	198.09	10045.88	8.65	1	2.285
Cu2p3+	931.65	19426.48	2.96	1	16.73
CuLMM	570.8	64194.92	0	0	1
N1s	399.59	20331.22	23.25	1	1.8
O1s	531.48	19815.02	14.44	1	2.93
S2p	164.03	15370.1	17.99	1	1.67

AMT 0.01M/H_2O, corroded copper





AMT 0.01M/H_2O, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.69	16328.19	32.71	1	1
Cl2p	198.09	10045.88	8.65	1	2.285
Cu2p3+	931.65	19426.48	2.96	1	25.39
CuLMM	570.8	64194.92	0	0	1
N1s	399.59	20331.22	23.25	1	1.8
O1s	531.48	19815.02	14.44	1	2.93
S2p	164.03	15370.1	17.99	1	1.67

AMT 0.01M/EtOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	286.16	2702.15	28.35	1	1
Cl2p	198.02	809.85	3.65	1	2.285
Cu2p	932.32	27250	14.32	1	25.39
CuLMM	570.68	8765.37	0	0	1
N1s	399.57	4610.7	27.6	1	1.8
O1s	531.92	980.32	3.74	1	2.93
S2p	164.08	3642.22	22.33	1	1.67

BTA (N/3): Cu= 0.6
O:Cu =0.3
Cl:Cu= 0.3

BTA 0.1M + AMT 0.01M/ H_2O

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	283.98	32405.39	58.6	1	1
Cl2p	197.08	2074.39	1.61	1	2.285
Cu2p3+	931.69	32807.89	4.51	1	16.73
CuLMM	570.33	26570.97	0	0	1
N1s	399.08	27279.4	28.16	1	1.8
O1s	531.31	2024.3	1.33	1	2.93
S2p	163.45	5472.36	5.78	1	1.67

BTA 0.1 + AMT 0.01/ EtOH corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.17	30768.11	45.52	1	1
Cl2p	197.37	2857.6	1.82	1	2.285
Cu2p3+	931.92	79724.93	8.97	1	16.73
CuLMM	570.29	44654.48	0	0	1
N1s	399.06	27677.91	23.37	1	1.8
O1s	531.53	8653.2	4.66	1	2.93
S2p	163.47	18110.51	15.66	1	1.67

BZA 0.1M/EtOH, clean copper-
This sample had S2p, Na and Ca. Not considered in the quant table-error in the analysis.

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.88	6613.77	35.8	1	1
Ca2p	347.41	2989.49	0	0	5.07
Cu2p	932.53	8250.17	2.24	1	25.39
Cu2p A	934.27	4473.94	0	0	25.39
CuLMM	569.59	8142.01	0	0	1
N1s	399.93	1681.4	5.2	1	1.8
Na1s	1071.68	26173.72	0	0	8.52
O1s	531.83	28815.45	56.76	1	2.93
S2p	168.94	2929.9	0	0	1.67

BZA 0.1M/EtOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.68	4714.86	51.52	1	1
Cl2p	199.75	2301.27	10.81	1	2.285
Cu2p	930.04	29943.49	16.37	1	25.39
CuLMM	567.84	7582.68	0	0	1
N1s	398.42	1303.79	8.13	1	1.8
O1s	529.15	3314.11	13.17	1	2.93

BTA0.1M + BZA 0.1M/EtOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.6	13146.82	67.97	1	1
Cl2p	198.16	124.11	0.28	1	2.285
Cu2p3+	935	8873.86	3.49	1	16.73
CuLMM	570.52	5729.83	0	0	1
N1s	399.8	9310.63	27.48	1	1.8
O1s	531.89	415.97	0.78	1	2.93

BTA 0.25M + ETH 0.1M, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.55	8683.02	66.97	1	1
Cl2p	199.12	38.51	0.13	1	2.285
Cu2p2+	934.81	6765.42	2.62	1	25.39
CuLMM	570.65	5224.27	0	0	1
N1s	399.49	6633.67	29.2	1	1.8
O1s	531.99	383.52	1.08	1	2.93

ETH 0.1M/EtOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF	
C1s	284.63	4430.9	35.06	1	1	
Cl2p	196.99	5623.81	19.13	1	2.285	
Cu2p	933.52	24320.3	9.65	1	25.39	
Cu2p A	931.63	1559.39	0	0	25.39	
CuLMM	569.95	13865.37	0	0	1	
N1s	398.61	3369.95	15.22	1	1.8	
O1s	530.15	7278.98	20.95	1	2.93	

BTA 0.1M + ETH 0.1M/H2O, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.61	9906.13	67.23	1	1
Cl2p	198.06	877.84	2.56	1	2.285
Cu2p32+	934.76	3284.29	1.7	1	16.73
CuLMM	570.71	10888.33	0	0	1
N1s	399.8	6711.84	26	1	1.8
O1s	532	1018.1	2.51	1	2.93

0.1M BTA + 0.1M ETH/eth, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.82	11975.36	68.71	1	1
Cl2p	201.7	2.76	0.01	1	2.285
Cu2p2+	935.22	383.88	0.11	1	25.39
cUlmm	570.61	6562.81	0	0	1
N1s	400.11	8899.55	29.15	1	1.8
O1s	531.45	970.96	2.03	1	2.93

BTA 0.25M + ETH, eth, corroded

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
Cu2p2+	934.8	6765.42	2.62	1	25.39
C1s	284.6	8683.02	66.97	1	1
N1s	399.5	6633.67	29.2	1	1.8
Cl2p	199.1	38.51	0.13	1	2.285
O1s	532	383.52	1.08	1	2.93
CuLMM	570.7	10901.5	0	0	1
Cu2p A	955	2974.87	0	0	25.39
Cu2p B	962.7	2048.72	0	0	25.39
Cu2p C	943.3	3468.81	0	0	25.39
Cu2p D	931.5	775.38	0	0	25.39

KI 0.1M /H_2O on corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.66	3284.82	11.81	1	1
Cl2p	198.08	228.3	0.35	1	2.285
Cu2p	932.24	43486.52	7.83	1	25.39
CuLMM	569.79	22640.29	0	0	1
I3d	619.28	13784.54	54.39	1	1
K2p	292.48	3516.2	3.19	1	3.97
K2s	377.48	1369.06	2.22	1	2.27
N1s	399.83	613.23	1.26	1	1.8
O1s	531.09	14484.97	18.95	1	2.93

KEX 0.1M, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
S2p	161.77	9512.98	41.37	1	1.67
O1s	532.62	7622.93	20.66	1	2.93
K2s	375.11	1053.17	0.28	1	2.27
K2p	286.13	2156.6	4.05	1	3.97
CuLMM	569.78	354281.8	0	0	1
Cu2p	931.7	728819.8	21.69	1	25.39
Cl2p	195.11	360.74	1.15	1	2.285
C1s	284.38	1450.92	10.8	1	1

BTA 0.1M + KEX 0.1M, clean copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.6	8841.38	51.83	1	1
Cl2p	199.88	68.95	0	0	2.285
Cu2p	935.66	4025.76	1.18	1	25.39
CuLMM	572.6	2477.72	0	0	1
K2p	292.85	6982.8	10.33	1	3.97
K2s	377.31	2620.53	6.91	1	2.27
N1s	398.76	5488.53	18.36	1	1.8
O1s	532.06	3058.47	6.53	1	2.93
S2p	165.3	1414.37	4.85	1	1.67

BTA 0.25M + PMT 0.1M/etOH, corroded copper

Name	Peak BE	Area (P) CPS.eV	At. %	Q	SF
C1s	284.61	9774.32	57.85	1	1
Cl2p	197.86	607.73	1.55	1	2.285
Cu2p3+	931.65	19426.48	8.74	1	16.73
CuLMM	571.09	7241.1	0	0	1
N1s	400.44	7184.17	24.27	1	1.8
O1s	532.18	1041.54	2.24	1	2.93
S2p	162.58	1548.29	5.35	1	1.67

Appendix 7